Appendix C
Computation of Detection and Quantitation Limits

INTRODUCTION

This appendix supports the Technical Support Document (TSD) for EPA's peer review of detection and quantitation concepts. It presumes that the reader has read Chapters 3 - 5 of the TSD.

This appendix compares detection and quantitation limits computed from data gathered by EPA. The comparison shows that, in general, detection limits derived from a single concentration such as EPA's MDL are, on average, approximately the same as detection limits derived from similar concepts such as the ACS LOD and LOQ and ISO/IUPAC CRV and MDV, and are approximately three times lower than a single-laboratory variant of ASTM's IDE; and that all quantitation limit concepts, such as EPA's ML, the ACS and ISO/IUPAC LOQ, and a single-laboratory variant of ASTM's IQE, produce approximately the same quantitation limits.

BACKGROUND

The regulated industry has been commenting on EPA's method detection limit (MDL; see the definition at 40 CFR 136, appendix B) since 1985 and on EPA's minimum level of quantitation (ML; see, e.g., the definition in the glossary at the end of EPA Method 1631C promulgated at 40 CFR 136, appendix A) since about 1987. In the early 1990s members of the regulated industry community began providing suggestions for alternate detection and quantitation limit concepts, most notably the compliance monitoring detection level (CMDL), compliance monitoring quantitation level (CMQL) and the alternate minimum level (AML). Most recently the industry community has advanced concepts for an interlaboratory detection estimate (IDE) and interlaboratory quantitation estimate (IQE) through ASTM-International (ASTM).

In response to industry's comments, EPA began a data gathering activity designed to allow evaluation of the various detection/quantitation limit concepts. The data would be used to characterize measurement variability versus concentration for the analytes most commonly measured in, and the analytical technologies most commonly employed for, environmental measurements.

SETTLEMENT AGREEMENT

In October of 2000, EPA signed an agreement associated with promulgation of EPA Method 1631 to settle a lawsuit brought by certain members of the regulated industry (the "Settlement Agreement"). The Settlement Agreement required EPA to, among other things, reassess detection and quantitation limit concepts, perform a peer review of the reassessment, and if warranted, propose changes to the MDL and ML or propose alternate concepts. This document supports EPA's reassessment.

EPA'S APPROACH TO ESTABLISHING DETECTION AND QUANTITATION LIMITS IN ANALYTICAL METHODS

The Engineering and Analysis Division (EAD) within EPA's Office of Science and Technology develops analytical methods for use in EPA's Clean Water Act (CWA) programs. In developing these methods, EAD first conducts a single-laboratory study in which an MDL and ML are determined followed by multiple single-laboratory studies in which the MDL and ML are either verified or if necessary, revised. Then, if resources, time, and applications of the method warrant, an interlaboratory study is conducted in which the MDL and ML are further verified or, if necessary, revised. To establish

that an MDL is realistic, EAD generally selects the highest MDL from among the MDLs determined by laboratories in the various studies or that can be verified by laboratories in the studies. For example, EPA determined the MDL in Method 1631 (mercury by cold-vapor atomic fluorescence) as 0.05 ng/L in a single laboratory and revised this MDL to 0.2 ng/L based on multiple single-laboratory studies. All laboratories verified the MDL of 0.2 ng/L in an interlaboratory study. Thus, although critics of the MDL have complained that the MDL is a single-laboratory concept that is highly variable and produces unrealistically low MDLs, the process used by EAD to establish the MDL and resulting ML is conservative and protects against unrealistically low MDLs and MLs.

EPA'S VARIABILITY VERSUS CONCENTRATION STUDIES ("EPISODE 6000")

In 1997 and 1998, EPA conducted a study of variability vs. concentration for a number of analytical methods. Six laboratories were employed for the analyses; each analyte and method combination was tested by one of these laboratories. Details of the study design are described in EPA's *Study Plan for Characterizing Variability as a Function of Concentration for a Variety of Analytical Techniques* (July 1998). Based on the sampling episode number assigned to the study by the EPA Sample Control Center, the study and results have become known as the Episode 6000 study and data.

The analytes and analytical techniques studied were:

- Total suspended solids (TSS) by gravimetry,
- Metals by graphite furnace atomic absorption spectroscopy (GFAA),
- Metals by inductively-coupled plasma atomic emission spectrometry (ICP/AES),
- Hardness by ethylene diamine tetraacetic acid (EDTA) titration,
- Phosphorus by colorimetry,
- Ammonia by ion-selective electrode,
- Volatile organic compounds by purge-and-trap capillary column gas chromatography with a photoionization detector (GC/PID) and electrolytic conductivity detector (GC/ELCD) in series,
- Volatile organic compounds by gas chromatography with a mass spectrometer (GC/MS),
- Available cyanide by flow-injection/ligand exchange/amperometric detection,
- Metals by inductively-coupled plasma spectrometry with a mass spectrometer (ICP/MS),

In the study, an initial (range finding) MDL was determined for each combination of analyte and analytical technique using a revised draft of the MDL procedure. The revised draft had three significant changes: 1) the definition was more closely conformed to the MDL procedure; 2) optional iterative step 7 of the MDL procedure was made mandatory; and 3) the spike concentration to MDL ratio was reduced from 5 to 3 in an attempt to narrow the resulting MDL. During data gathering two laboratories complained that the reduction in spike to determined MDL ratio from 5 to 3 caused a large number of iterations and stated that 5 was more reasonable. Subsequently, EPA returned to the spike to MDL ratio of 5 published in the 40 CFR 136, Appendix B procedure.

After determining the initial MDL, each laboratory analyzed 7 replicates of samples spiked at concentrations of 100, 50, 20, 10, 7.5, 5.0, 3.5, 2.0, 1.5, 1.0, 0.75, 0.50, 0.35, 0.20, 0.15, and 0.10 times the initial MDL. In a few instances laboratories analyzed more than 7 replicates. Results associated with the replicate analyses at each concentration level were obtained, as often as possible, using the same calibration that was used in determining the initial MDL. Where laboratory reports indicated that multiple calibrations were conducted, the association between each result and its calibration was used in the data analysis.

Spiked aqueous solutions were analyzed in order from the highest concentration (100 times the MDL) to the concentration at which 3 or more non-detects (zeros) were encountered among the 7

replicates, or the lowest concentration specified (0.1 times the MDL), whichever occurred first. This analysis order (1) minimized carryover that could occur in some methods if a low-concentration sample had followed a high-concentration sample (as may happen when samples are analyzed in random order), and (2) prevented collection of a large number of zeros if the signal disappeared.

A variant of the iterative MDL procedure was used for organic compounds determined by chromatographic methods. Methods for organics normally list many (15 to 100) analytes, and the response for each analyte is different. Therefore, to determine an MDL for each analyte, the concentration of the spike would need to be inversely proportional to the response. Making a spiking solution with 15 to 100 different concentrations is cumbersome and error prone. The approach used in the study was to run 7 replicates at decreasing concentrations until signal extinction, then select the concentration(s) appropriate for the MDL for each analyte according to the MDL procedure. In some cases the laboratories selected the concentrations, in others cases, EPA did. This approach was generally applied for organics analysis. However, laboratories also had the option of using some combination of monotonically decreasing concentrations described above and a few selected concentrations to achieve the desired spiking levels.

DATA ANALYSIS

Data from the study were used to evaluate detection and quantitation limit concepts that employ a point estimate or employ a model of variability versus concentration. Concepts that were evaluated and that employ a point estimate were the:

- EPA method detection limit (MDL) and minimum level of quantitation (ML),
- American Chemical Society (ACS) limit of detection (LOD) and limit of quantitation (LOQ), and
- International Standards Organization/International Union of Pure and Applied Chemistry (ISO/IUPAC) critical value (CRV), detection limit (also termed "minimum detectable value" (MDV)), and LOQ.

Concepts that were evaluated and employ a model of variability versus concentration were the ASTM interlaboratory detection estimate (IDE) and interlaboratory quantitation estimate (IQE).

COMMONALITY OF CONCEPTS

The EPA, ACS, and ISO/IUPAC concepts are all multiples of the standard deviation of either replicate measurements of a blank or of the lowest spike concentration that produces positive (non-zero) results for all 7 replicates. Although some would argue that this difference is significant, in practice they are functionally analogous because a non-zero result is needed to compute any concept (a zero result will return zero as the detection or quantitation limit).

Other subtle distinctions are that (1) ISO/IUPAC suggest a false positive rate of 5 % ($\alpha = 0.05$) for the CRV and MDV, whereas EPA specifies a false positive rate of 1 % ($\alpha = 0.01$) for the MDL and (2) the EPA MDL was calculated by pooling data from two concentration levels after determining that the variabilities of the two concentration levels are not significantly different (as stipulated in step 7 of the revised MDL procedure), thereby increasing the degrees of freedom to 12 from the 6 used in computation of the ISO/IUPAC CRV and ACS LOD. The consequence of distinction 1) is that a concept with a higher allowed false positive rate ($\alpha = 0.05$) will produce a lower detection limit than a concept with a lower false positive rate ($\alpha = 0.01$). The consequence of distinction 2) is that a detection limit resulting from pooling at two levels will be lower and more stable than a detection limit at a single level (given the same variability at each level) because the degrees of freedom are increased in the *t* statistic.

The ACS and ISO/IUPAC concepts specify replicate measurements of a blank. In computing detection and quantitation limits from the Episode 6000 data, if the blank returned non-zero results, the concepts were computed using replicate measurements of the blank. If the blank returned a zero result in any of the 7 measurements, the lowest spike concentration (or, in the case of the MDL, two lowest spike concentrations) that produced a non-zero result was used for computation of all concepts. This simplification condensed the EPA MDL and the ACS LOD to a single concept subsequently termed the EPA/ACS DL. Similarly, the EPA ML and ACS LOQ were condensed to a single concept, termed the EPA/ACS QL.

The remaining single-point concepts were the ISO/IUPAC CRV, MDV, and LOQ. The ISO/IUPAC CRV differs from the EPA/ACS DL because of its suggested use of a false positive rate of 5% ($\alpha = 0.05$) versus use of a false positive rate of 1 % ($\alpha = .01$) in the EPA/ACS DL. The ISO/IUPAC MDV also differs from the EPA/ACS DL because of (1) its suggested use of a false positive rate of 5 % ($\alpha = 0.05$), (2) its false negative rate of 5 % ($\beta=0.05$), and (3) recovery correction (estimated using a linear regression). Therefore, the ISO/IUPAC CRV and MDV were each treated separately (were not combined with another concept) from the other detection limit concepts in the data analysis. The ISO/IUPAC LOQ is also different from the other quantitation limit concepts and was treated separately from these concepts.

The ASTM IDE and IQE were treated separately because they are constructed by fitting a model to variability versus concentration data, rather than being derived from the standard deviation of replicate measurements of a single concentration, as are the EPA, ACS, and ISO/IUPAC concepts. Similar to some of the ISO/IUPAC concepts, the ASTM IDE and IQE include protection against false negatives and recovery correction. The IQE, but not IDE, also includes an added correction for the bias associated with an estimate of the true standard deviation at each concentration. In the context of the IQE, the word "bias" means the amount by which the estimated sample standard deviation is low compared to the true population standard deviation, and should not be confused with common use of the word "bias" in an analytical measurement.

SINGLE-LABORATORY VARIANTS OF INTERLABORATORY CONCEPTS

EPA's Episode 6000 database contains single-laboratory data because of the prohibitive expense that would have been incurred in gathering interlaboratory data. Because the EPA, ACS, and ISO/IUPAC concepts are single-laboratory concepts, and the ASTM IDE and IQE are interlaboratory concepts, the ASTM concepts could not be computed using the single-laboratory data in the Episode 6000 studies. To solve this problem, single-laboratory variants of the IDE and IQE were used. These single-laboratory variants were termed the SL-IDE and SL-IQE for "single-laboratory IDE" and "single-laboratory IQE." The SL-IDEs and SL-IQEs were constructed using the overall standard deviation within a single laboratory at each concentration rather than the overall standard deviation across all laboratories at each concentration.

ATTEMPTED APPLICATION TO INTERLABORATORY DATA

EPA attempted to apply the various concepts to interlaboratory study data in response to a request by the Petitioners to the Settlement Agreement and so that detection and quantitation limits could be compared. However, because the EPA, ACS, and ISO/IUPAC concepts are single-laboratory concepts whereas the ASTM concepts are interlaboratory concepts, it was not possible to compute directly comparable detection and quantitation limits from the same data.

What was possible was to compare detection and quantitation limits produced by EPA and the Electric Power Research Institute (EPRI) for the EPA Method 1631 and EPA Method 1638

interlaboratory study data. Although the resulting detection and quantitation limits are single- or interlaboratory, as appropriate to the particular concept; i.e., apples versus oranges, their magnitudes are informative. The EPRI detection and quantitation limits are from EPRI reports of the results of the Method 1631 and Method 1638 studies.

COMPUTATIONS

All computations were carried out using Statistical Analysis System (SAS) version 8.01. The equations for all concepts were programmed into the SAS software by a senior statistician, with assistance from senior analysts. There is some ambiguity in the IUPAC/ISO and ASTM detection and quantitation limit concepts and in interpretation of results from the ASTM concepts. Several formulas are given in the IUPAC/ISO documentation, but none are defined to be the official ISO/IUPAC detection and quantitation limit concepts. Therefore, calculations for the CRV, MDV, and LOQ were chosen because they were most representative of Lloyd Currie's definitions of a critical value, detection limit and quantitation limit. The specific equations used are on the CD-ROM that supports this Appendix. Ambiguity in results from the ASTM concepts is attributable to the subjective nature of interpreting residual plots for each analyte. To resolve this issue, IDE and IQE models were chosen using significance tests for slope and curvature.

References used for the IUPAC/ISO concepts were those published by Currie in *Pure and Applied Chemistry* **67**:10, 1699-1723 (1995) as updated by *Analytica Chimica Acta* **391** 105-126 (1999). Where needed, the ASTM concepts were programmed as single-laboratory variants of the Practices D 6091 (IDE) and D 6512 (IQE). EPA has included the SAS program code on the CD-ROM that supports this document.

DATA SETS EVALUATED

EPA computed EPA/ACS detection limits and quantitation limits; ISO/IUPAC CRVs, MDVs and LOQs; and single-laboratory variants of ASTM IDEs (SL-IDEs) and IQEs (SL-IQEs) for the Episode 6000 data. EPA also computed IDEs and IQEs for the Method 1631 and 1638 interlaboratory study data.

DATA SETS NOT EVALUATED

The Petitioners and Intervenor to the Settlement Agreement provided the list of data sets shown in Table 1 and suggested that EPA evaluate detection/quantitation limit concepts using the data sets on the list. However, in reviewing the data sets suggested, EPA determined that many were developed for characterizing the behavior of an analyte or analytes across the analytical range of a method, rather than in the region of detection and quantitation, while others did not result from the IDE and IQE procedures. For example, any data set developed prior to the advent of the IDE and IQE would be inappropriate because there could not have been an estimate of IDE_0 or IQE_0. This eliminates all data sets in Table 1 except the EPA/EPRI Method 1631 and Method 1638 data set, and the MMA 2001-2 data set. It is possible that some value in one or more of the data sets developed prior to the advent of the IDE and IQE would fortuitously meet the IDE/IQE criteria. But the IDE and IQE can be circular; i.e., once developed from a given data set there may be a value in the data set than can be construed to meet the criteria. The point is that data sets developed without following the IDE and IQE procedures, particularly without making an *a priori* estimate of IDE_0 or IQE_0, do not meet the requirements of the IDE and IQE procedures, regardless of whether the data in them can be construed to have met those requirements after the fact.

In addition, these data sets do not lend themselves to the comparisons used in this report because 1) they contain interlaboratory data that cannot be reduced to single-laboratory data without treating each

laboratory separately[1] and 2) the developers of these data sets did not apply EPA's procedure and measurements for establishing an MDL and ML, so an MDL and ML could not be determined for making comparisons (see the section titled "EPA's Approach to Establishing Detection and Quantitation Limits in Analytical Methods").

Further, the EPA 6000 data set is comprehensive in coverage of analytes, analytical techniques, and a concentration range from 0.1 to 100 times the MDL, whereas the data sets suggested by Petitioners focus on metals, one organic analyte (PCBs), and concentrations across the analytical range of the method. The range of data used for construction of an IDE or IQE is particularly important. As detailed in the discussion of the "Effect of number and spacing of concentrations for determination of the SL-IDE and SL-IQE" below, including data across the analytical range in calculation of an SL-IDE significantly raises the SL-IDE.

As stated in the section titled "Attempted Application to Interlaboratory Data" EPA used the EPA Method 1631 and 1638 data sets in computations of detection and quantitation limits, with the qualifiers given in that section. The EPA Method 1631 and Method 1638 data sets were the only data sets suggested by the Petitioners that were used.

RESULTS OF COMPUTATIONS

Detection and quantitation limits are presented in a set of tables for the Episode 6000 study and a single table for the Method 1631 and Method 1638 studies. Within the Episode 6000 data set, results for detection limits are compared followed by results for quantitation limits. Within the comparison of limits (detection or quantitation), the first table compares the actual limits followed by a table of ratios between limits. These tables are followed by a rank comparison table, making a total of five tables for this data set.

EPISODE 6000 DATA

Table 2 compares detection limits produced by the four concepts (EPA/ACS DL; ISO/IUPAC CRV; ISO/IUPAC MDV; and ASTM SL-IDE) and Table 3 compares the ratio between these concepts, taking the EPA/ACS DL as reference. The ISO/IUPAC CRV was greater than the corresponding EPA/ACS DL for 26% of the analytes and methods. The median ratio of ISO/IUPAC CRV to EPA/ACS DL was significantly less than 1 based on the sign test with $\alpha = 0.05$ ($p<0.0001$). We believe that the major reason for the difference is the different Type I error rate for the two concepts ($\alpha = 0.01$ for the EPA/ACS DL and $\alpha = 0.05$ for the ISO/IUPAC CRV).

The median ratio between the ISO/IUPAC MDV and the EPA/ACS DL is 1.2; i.e., the ISO/ IUPAC MDV is a median of 1.4 times higher than the EPA and ACS concepts. The ISO/IUPAC MDV was greater than the corresponding EPA/ACS DL for 57% of the analytes and methods. The median ratio of ISO/IUPAC MDV to EPA/ACS DL did not differ significantly from 1 based on the sign test with $\alpha = 0.05$ ($p=0.055$). The likely reason that the two concepts do not yield significantly different results is that the correction for false negatives and recovery correction in the MDV ($\beta = 0.05$) are counteracted by the smaller Type I error rate for the EPA/ACS DL.

[1] Treating each laboratory separately would lead to further ambiguities because results from some laboratories could produce detection and quantitation limits greater than the single-concentration limits whereas results from other laboratories could produce detection and quantitation limits less than the single-concentration limits. Given the variability of the data, such an outcome would be virtually assured and would provide no further useful information.

The median ratio between the ASTM SL-IDE and the EPA/ACS DL is 2.9; i.e., the single-laboratory variant of the ASTM IDE is a median of 2.9 times higher than the EPA and ACS concepts. The SL-IDE was greater than the corresponding EPA/ACS DL for 91% of the analytes and methods. The median ratio differed significantly from 1 based on the sign test with $\alpha = 0.05$ ($p<0.0001$). The reason(s) for the difference could not be determined easily because of the number of confounding factors included in the ASTM SL-IDE.

Table 4 compares quantitation limits produced by the three concepts (EPA/ACS QL; ISO LOQ; and ASTM SL-IQE) and Table 5 compares the ratio between these concepts taking the EPA/ACS QL as reference. The median ratio between the ISO/IUPAC LOQ and the EPA/ACS QL is 0.92, and the median ratio between the ASTM SL-IQE and the EPA/ACS QL is 1. The ISO LOQ and ASTM SL-IQE are greater than the corresponding EPA/ACS QL for 43% and 51% of the analytes and methods, respectively. The median ratio did not differ significantly from 1 based on the sign test at $\alpha = 0.05$ (LOQ: $p=0.062$; SL-IQE: $p=0.78$) The reason(s) why the ASTM SL-IQE, ISO LOQ, and the EPA/ACS QL produce nearly identical limits could not be determined easily because of the number of confounding factors included in the ASTM SL-IQE.

Some of the differences or similarities in median quantitation limits may be accounted for by rounding in the ML procedure, although the rounding should average over the large number of analytes examined.

Table 6 gives the frequency comparisons for the detection and quantitation limits; i.e., the frequency with which each concept produced the highest or lowest quantitation limit.

EPA/EPRI METHOD 1631 AND 1638 INTERLABORATORY METHOD VALIDATION STUDY DATA

Table 7 compares detection and quantitation limits computed from data generated in the Method 1631 and Method 1638 interlaboratory studies. MDLs and MLs are those listed in EPA Methods 1631 and 1638. EPA computed IDEs and IQEs for the purpose of preparing this report. IDEs and IQEs computed by EPRI are from the EPRI reports on EPA Method 1631 and Method 1638 studies.

In reviewing these data it must be recognized that the EPA MDLs and MLs are the result of selecting the highest MDL in EPA's single-laboratory studies or among MDLs from the interlaboratory study, whereas the IDEs and IQEs are the result of a statistical process that includes recovery correction, correction for bias in the sample standard deviation (IQE only), allowance for prediction and tolerance intervals, interlaboratory variability, and model selection. The most significant reason for the instances of a large disparity between the EPA-determined IDEs/IQEs and the EPRI-determined IDEs/IQEs is model selection. EPA selected the model based on a strict application of the IDE and IQE procedures by a senior statistician. For those instances in which EPA and EPRI selected the same model, the IDEs and IQEs are nearly the same.

Table 8 compares IDEs resulting from the four main model types described in the ASTM IDE and IQE procedures. IDEs resulting from the constant model were the highest for all analytes. IDEs resulting from the other three models were almost equal for some analytes (lead, for example), and differed by more than an order of magnitude for others (mercury, for example). For two analytes, the IDE estimated using the linear model was negative. This was due to a negative intercept estimate in the precision model. The ASTM IDE and IQE procedures dictate that the linear model should not be used in this situation. No IDE could be calculated using the hybrid model for silver, because the IDE did not

converge to a single value using the calculated model for precision. This failure to converge is consistent with results for this analyte presented by EPRI.

DISCUSSION

Negative detection limits for the ISO/IUPAC MDV

The calculated MDV was negative for 26 analytes in the Episode 6000 data. Negative MDVs are attributable to the use of a regression model to estimate recovery at each concentration. The standard errors and correlation of the regression parameters are included in the calculation of the MDV. Analytes for which the MDV was negative seemed to coincide with an unusually large standard error of the regression intercept, which generally occurred when the estimated intercept was strongly negative. The large standard error of the intercept was likely due to extrapolating the recovery model to zero concentration; the error around a regression line is greatest for concentrations furthest away from the mean spike level. The effect of this extrapolation may also be seen in the Episode 6000 data. No negative results were used in the MDV and LOQ calculations, yet the median recovery intercept for these analytes was equal to -0.10. The standard errors of the intercept and slope estimates were generally high (intercept median=0.25, slope median=0.010), and therefore the estimated intercept and slope terms were frequently not significantly different from 0 and 1, respectively (intercept: not different from zero for 166 analytes/methods; slope not significantly different from 1 for 106 analytes; both intercept and slope not significant for 78 analytes). Because the recovery model parameters are not significant for the majority of analytes, and both the estimated slope and the standard errors of the slope and intercept are included in the calculation of the MDV and LOQ, the inclusion of the recovery model estimates may bias the calculated limits, to the point that the resulting MDV can be negative.

Effect of number and spacing of concentrations for determination of the SL-IDE and SL-IQE

Tests in the Episode 6000 studies were conducted at 16 concentration levels. The IDE procedure suggests 5 concentration levels. Based on statistical theory we would the expect the number and spacing of concentration levels to affect the outcome, with a larger number of concentrations producing a more reliable estimate. We used the Episode 6000 data set to test this hypothesis.

The IDE procedure suggests spike concentrations at 0.5, 1.0, 2, 4, and 8 times an initial estimate of the IDE (IDE_0). IDE_0 is estimated at 10 times the standard deviation of replicates of a blank or the lowest level that can be measured. EPA's Episode 6000 database contain results of analysis of 7 replicates at 16 concentration levels from 0.1 to 100 times the initial estimate of the MDL (a factor of 1000). Between 0.1 and 10 times the MDL, the data are spaced a factor of approximately 1.5 apart. Above 10 times the MDL, the data are spaced at 10, 20, 50 and 100 times the MDL. The reason for the narrow spacing between 0.1 to 10 times the MDL was to attempt to allow more precise characterization of variability in the region of the MDL.

The SL-IDEs and SL-IQEs in Tables 2 and 4, respectively, were computed and reported using all 16 concentration levels because data were available at all of these levels. However, to determine the effect of the IDE procedure, a separate data analysis was performed. In this separate analysis, concentration levels were limited to a total of 5, and the 5 levels were selected to be as consistent as possible with the levels specified in the IDE procedure; i.e., at 5, 10, 20, 40, and 80 times the standard deviation of replicate measurements of a blank or the lowest level at which measurements could be made. The statement "lowest level at which measurements can be made" can be interpreted to mean inclusion or exclusion of results containing zeros and/or negative numbers. For purposes of the evaluation,

concentrations that produced results containing a zero or negative number were excluded; i.e., the lowest concentration that contained no zeros or negative numbers was chosen as the concentration at which the standard deviation would be calculated for the purpose of estimating IDE_0 and IQE_0. Although some statisticians may argue that zeros and negative numbers should be included, nearly all analytical chemists would eliminate such numbers because they have no physical meaning.

The SL-IDE was calculated after selecting the levels based on IDE_0 and the results were compared to results produced when all 16 levels were included in calculating the SL-IDE. Results are summarized in Table 9. This table shows that the median 16-point IDE is approximately 1.3 times greater than the median 5-point IDE. For those instances in which the same model was chosen (108 out of 198), the median 16-point IDE was approximately 1.4 times higher than the median 5-point IDE, which was significantly different from 1.0 based on a sign test ($p < 0.0001$). For those instances in which a different model was chosen (90 out of 198), the median 16-point IDE was approximately 0.9 times the median 5-point IDE, which was not significantly different from 1.0 ($p = 0.83$). Because the choice of model can have a confounding effect on any differences between 16-point and 5-point SL-IDEs, the focus should be on the instances in which the same model was chosen. For these instances, the results indicate that only data in the region of detection and quantitation should be used to establish a detection or quantitation limit.

Parallel reasoning can be applied to the IQE, because IQE_0 is specified and the IQE is developed in a way analogous to that for the IDE.

RSD AT THE ML IN THE EPISODE 6000 STUDY

The minimum level of quantitation (ML) is directed at the level at which 10% relative standard deviation (RSD) is attained. However, because the ML is not established at exactly 10% RSD, but is determined by multiplying the standard deviation that is obtained in determination of an MDL by 10 (as recommended by both ACS and Currie for ACS and ISO/IUPAC LOQs), the resulting RSD may not be 10%. The Episode 6000 data provided the opportunity to determine the actual value of the RSD at the ML. Results of the determination showed that the overall median RSD at the ML across all 198 analytes in the Episode 6000 study was 7 %, and the median RSD per analytical technique ranged between 6 and 16 percent by analytical technique for analytes in the 10 analytical techniques in the study. For 126 of the 198 individual analytes, the RSD fell between 5% and 15%. For the majority of the analytes that fell outside this range (56 out of 72), the RSD was less than 5%.

There was a spike concentration at the ML for approximately 80 percent of the analytes in the Episode 6000 study so the RSD could be determined directly for these analytes. For a few analytes there was not a spike concentration at the ML, and the RSD was determined by interpolation between spike levels for these analytes. However, for 82 out of 198 analytes, the concentration at the ML was below the range of the data; i.e., below the lowest spike concentration that returned non-zero and non-negative results. These instances were for organic analytes determined by EPA Methods 502.2 and 524.2. The reason that these low values occur is because hardware and/or software thresholds in chromatographic instruments that are set to eliminate spurious noise signals also filter out responses at low concentrations. For instances in which this occurred, the ML was calculated as the lowest concentration at which non-zero and non-negative results were not reported, and the RSD was calculated at this concentration. The median RSD for these analytes was 5%, compared to a median of 9% where this did not happen.

CONCLUSIONS

The comparisons of detection and quantitation limits show high variability among the limits calculated using the different concepts, even with data containing 7 replicates at 16 concentration levels (see the summary statistics at the end of Tables 3 and 5, Table 6, and the final conclusion below). The net effect is that the systematic differences among detection and quantitation limits produced by the various concepts are overwhelmed by variability; i.e., there is a small systematic difference among the concepts but great variability in the detection and quantitation limits for a given analyte. This result is not surprising given the variability of data in the region of detection and quantitation. However, it is difficult to postulate a solution to the problem. Gathering more data in the region of detection and quantitation would appear to be a solution, but 91 data points were gathered for each analyte in the region between 0.1 and 10 times the MDL in the Episode 6000 studies, and it is unlikely that any organization could afford to gather even this amount of data for determination of a detection limit. Given the high degree of variability of the data, EPA's approach of conducting single-laboratory study to gain a first estimate, then multiple single-laboratory studies to verify or revise the estimate, then an interlaboratory study, where warranted, to further verify and revise the estimate, is a reasonable means of establishing detection and quantitation limits because of the checks and balances that occur at each step.

A second conclusion is that using a regression line to estimate a recovery correction at zero concentration causes great swings in the resulting detection and quantitation limits such as the ISO/ IUPAC MDV and LOQ. The estimated regression parameters for the recovery models were often not significant, and the inclusion of the estimated slope and the standard errors of the slope and intercept will therefore unnecessarily bias the calculated MDV and LOQ, such that the calculated MDVs may be negative (see Discussion section "Negative detection limits for the ISO/IUPAC MDV, and Table 2 for instances of negative detection limits"). The estimated recovery model used in calculating the IDE and IQE is also strongly affected by the chosen model of variability vs. concentration (see Table 8). Even though a linear regression is used to model recovery in each case, the weights used in the model are calculated based on the variability model, and can vary greatly when the number of concentrations used is low. For the Episode 6000 data, the median RSD of the recovery slopes from the four different models used in the IDE calculations for a given analyte and method was 5%. In addition, for 75 of the analytes and methods (38%), at least one estimated recovery slope was greater than 1, and at least one was less than 1. This suggests that the method could be considered to be high biased (and the final IDE and IQE would be decreased by the recovery correction) and low biased (and the final IDE and IQE increased) for the analyte, depending on the chosen precision model. For many analytes the slopes were not significantly different from 1, suggesting that a recovery correction may not be appropriate at all. This is in addition to the philosophical issue as to whether recovery correction is warranted. If there is to be a correction for recovery, it may be better to use some average or median value than a regression, or use a measured value near the region of interest.

A third conclusion is that further work will need to be done on the ASTM IDE and IQE before they can be used routinely, not only because of the complexity of the procedures, but also because of the ambiguity in determining that the correct model has been selected. (For the consequences of model selection, compare the IDEs and IQEs determined by EPA and EPRI in Table 7, and the IDEs calculated from the different model types in Table 8. Some differ considerably as a result of model selection in application of the IDE and IQE procedures by different statisticians.)

A fourth conclusion is that quantitation limit concepts such as EPA's ML and the ACS and ISO/ IUPAC LOQ that are directed 10% RSD actually produce RSDs that are in the range of the 10% intended (see the discussion in the Section titled "RSD at the ML in the Episode 6000 Study"). The median RSDs for each method in the Episode 6000 data set ranged from 6% to 16%, and 64% of the individual analyte RSDs fell between 5% and 15%.

Finally, a statement needs to be made about the overall philosophy behind the concepts. A natural progression through time is to refine any theory or concept. However, in the case of detection and quantitation in analytical chemistry (and as applied to other disciplines), the effort to further refine concepts may be futile, given the variability of the data that must be used with any concept. However, it is clear no concept produces the "right" answer. Different concepts allow for different sources of variability resulting in shifts in the magnitude of the limit. For the EPA, ACS, ISO/IUPAC, and ASTM concepts, the most significant causes of this shift appear to be 1) the false positive rate ($\alpha = 0.01$ or 0.05), 2) the allowance for false negatives ($\beta = 0.05$), 3) recovery correction, 4) correction for the bias in the calculated standard deviation (IQE only), 5) interlaboratory variability, and 6) model selection in the IDE and IQE.

Table 1. Data Sets Suggested by Petitioners

Data Set and Year	Analyte and Technology
AAMA 1996-7	Metals by ICP/AES (200.7)
AAMA 1996-7	Mercury by CVAA (245.2)
AAMA 1996-7	PCBs by GC/ECD (608.2)
MMA 2000-1	PCB 1216 and 1260 by GC/ECD
EPA/EPRI 1997-8	Mercury by CVAF (1631)
EPA/EPRI 1997-8	Metals by ICP/MS (1638)
EPRI 1987	Metals by GFAA (EPA 200)
EPRI 1990	Metals by ICP/AES (EPA 200.7)
EPRI 1994	Al, Be, Tl by GFAA (EPA 200)
EPRI 1996	Cd, As, Cr by GFAA (EPA 200)

Table 2. Comparison of Detection Limits (µg/L except where footnoted) for the Episode 6000 Data set

Analyte	Method	Procedure	EPA/ ACS DL	ISO CRV	ISO MDV	ASTM SL-IDE
1,1,1,2-tetrachloroethane	502.2	ELCD	0.041	0.028	0.054	0.028
1,1,1,2-tetrachloroethane	524.2		0.052	0.039	-0.030	0.206
1,1,1-trichloroethane	502.2	ELCD	0.012	0.009	0.017	0.035
1,1,1-trichloroethane	524.2		0.055	0.021	0.007	0.268
1,1,2,2-tce+1,2,3-tcp	502.2	ELCD	0.064	0.225	0.417	0.170
1,1,2,2-tetrachloroethane	524.2		0.132	0.131	0.139	0.377
1,1,2-trichloroethane	502.2	ELCD	0.024	0.055	0.103	0.026
1,1,2-trichloroethane	524.2		0.075	0.043	0.045	0.284
1,1-dichloroethane	502.2	ELCD	0.010	0.008	0.016	0.066
1,1-dichloroethane	524.2		0.033	0.020	0.018	0.206
1,1-dichloroethene	502.2	ELCD	0.038	0.013	0.032	0.193
1,1-dichloroethene	524.2		0.054	0.035	-0.030	0.278
1,1-dichloropropanone	524.2		5.184	3.146	5.657	6.032
1,1-dichloropropene	524.2		0.045	0.012	-0.020	0.247
1,2,3-trichlorobenzene	502.2	ELCD	0.048	0.308	0.599	0.122
1,2,3-trichlorobenzene	502.2	PID	0.057	0.301	0.623	0.114
1,2,3-trichlorobenzene	524.2		0.070	0.040	0.036	0.259
1,2,3-trichloropropane	524.2		7.328	0.046	0.042	1.206
1,2,4-trichlorobenzene	502.2	ELCD	0.022	0.189	0.393	0.077
1,2,4-trichlorobenzene	502.2	PID	0.070	0.221	0.471	0.124
1,2,4-trichlorobenzene	524.2		0.053	0.050	0.057	0.208
1,2,4-trimethylbenzene	502.2	PID	0.095	0.075	0.167	0.123
1,2,4-trimethylbenzene	524.2		0.012	0.009	0.017	0.129
1,2-dibromo-3-chloropropane	524.2		1.457	0.391	0.702	1.619
1,2-dibromoethane	502.2	ELCD	0.096	0.028	0.056	0.143
1,2-dibromoethane	524.2		0.127	0.117	0.175	0.289
1,2-dichlorobenzene	502.2	ELCD	0.035	0.073	0.144	0.053
1,2-dichlorobenzene	502.2	PID	0.033	0.024	0.054	0.147
1,2-dichlorobenzene	524.2		0.030	0.023	-0.010	0.112
1,2-dichloroethane	502.2	ELCD	0.017	0.017	0.032	0.037
1,2-dichloroethane	524.2		0.039	0.024	0.017	0.229
1,2-dichloropropane	502.2	ELCD	0.023	0.196	0.393	0.037
1,2-dichloropropane	524.2		0.056	0.031	0.029	0.221
1,3,5-tmb+4-chlorotoluene	502.2	PID	0.067	0.201	0.449	0.108

Table 2. Comparison of Detection Limits (µg/L except where footnoted) for the Episode 6000 Data set

Analyte	Method	Procedure	EPA/ ACS DL	ISO CRV	ISO MDV	ASTM SL-IDE
1,3,5-trimethylbenzene	524.2		0.011	0.008	0.009	0.117
1,3-dichlorobenzene	502.2	ELCD	0.035	0.048	0.104	0.100
1,3-dichlorobenzene	502.2	PID	0.093	0.134	0.297	0.123
1,3-dichlorobenzene	524.2		0.023	0.016	-0.010	0.126
1,3-dichloropropane	502.2	ELCD	0.016	0.071	0.135	0.045
1,3-dichloropropane	524.2		0.038	0.024	-0.010	0.170
1,4-dichlorobenzene	502.2	ELCD	0.026	0.101	0.198	0.054
1,4-dichlorobenzene	524.2		0.023	0.017	-0.040	0.110
1-chlorobutane	524.2		0.020	0.016	0.019	0.200
2,2-dichloropropane	524.2		2.376	0.103	-0.120	0.700
2-butanone	524.2		0.417	0.297	0.515	0.775
2-chlorotoluene	502.2	ELCD	0.108	0.162	0.318	0.184
2-chlorotoluene	502.2	PID	0.238	0.454	1.022	0.222
2-chlorotoluene	524.2		0.016	0.009	0.003	0.121
2-hexanone	524.2		1.316	0.148	0.234	0.815
2-nitropropane	524.2		0.901	0.275	0.457	0.965
4-chlorotoluene	502.2	ELCD	0.110	0.127	0.234	0.159
4-chlorotoluene	524.2		0.010	0.008	0.008	0.102
4-isopropyltoluene	524.2		0.010	0.008	0.005	0.102
4-methyl-2-pentanone	524.2		0.812	0.480	0.740	1.060
Acetone	524.2		0.859	0.440	0.806	2.025
Acrylonitrile	524.2		0.863	0.444	0.658	1.197
Allyl Chloride	524.2		0.032	0.026	0.010	0.203
Aluminum	1620		29.555	15.043	28.670	198.565
Aluminum	200.8		19.145	1.690	3.547	12.004
Ammonia as Nitrogen [1]	350.3		0.010	0.007	0.014	0.013
Antimony	1620		1.552	0.801	1.754	4.087
Antimony	200.8		0.178	0.003	0.007	0.018
Arsenic	1620		1.065	0.917	1.375	1.463
Arsenic	200.8		0.226	0.137	0.272	0.346
Barium	1620		1.702	1.337	1.831	1.762
Barium	200.8		0.033	0.029	0.061	0.079
Benzene	502.2	PID	0.030	0.043	0.099	0.077
Benzene	524.2		0.014	0.014	0.027	0.115

Table 2. Comparison of Detection Limits (µg/L except where footnoted) for the Episode 6000 Data set

Analyte	Method	Procedure	EPA/ ACS DL	ISO CRV	ISO MDV	ASTM SL-IDE
Beryllium	1620		0.528	0.339	0.408	0.428
Beryllium	200.8		0.007	0.004	0.006	0.019
Boron	1620		15.387	10.356	17.790	19.884
Bromobenzene	502.2	ELCD	0.131	0.093	0.187	0.729
Bromobenzene	502.2	PID	0.012	0.286	0.619	0.048
Bromobenzene	524.2		0.044	0.036	-0.050	0.175
Bromochloromethane	502.2	ELCD	0.013	0.016	0.032	0.462
Bromochloromethane	524.2		0.125	0.113	0.165	0.309
Bromodichloromethane	502.2	ELCD	0.004	0.016	0.032	0.064
Bromodichloromethane	524.2		0.043	0.026	0.023	0.182
Bromoform	502.2	ELCD	0.006	0.009	0.016	1.450
Bromoform	524.2		0.123	0.065	0.040	0.350
Bromomethane	502.2	ELCD	0.267	0.047	0.010	6.993
Bromomethane	524.2		0.068	0.055	0.060	0.238
Cadmium	1620		0.127	0.079	0.134	0.184
Cadmium	200.8		0.004	0.007	0.012	0.011
Calcium	1620		36.726	35.822	72.400	39.651
Carbon Disulfide	524.2		0.027	0.016	-0.030	0.203
Carbon Tetrachloride	524.2		0.038	0.027	-0.030	0.258
Carbontet+1,1-dcp	502.2	ELCD	0.029	0.028	0.060	0.062
Chloroacetonitrile	524.2		0.919	0.773	1.535	1.535
Chlorobenzene	502.2	ELCD	0.011	0.016	0.034	0.440
Chlorobenzene	502.2	PID	0.030	0.080	0.178	0.062
Chlorobenzene	524.2		0.025	0.022	0.016	0.119
Chloroethane	502.2	ELCD	0.108	0.006	0.004	2.492
Chloroethane	524.2		0.066	0.041	0.042	0.336
Chloroform	502.2	ELCD	0.043	0.410	0.758	0.031
Chloroform	524.2		0.036	0.027	0.025	0.203
Chloromethane	502.2	ELCD	0.070	0.090	0.240	0.204
Chloromethane	524.2		0.045	0.036	0.066	0.215
Chromium	1620		0.310	0.254	0.386	0.478
Chromium	200.8		0.073	0.062	0.125	0.393
Cis-1,2-dce+2,2-dcp	502.2	ELCD	0.013	0.017	0.034	0.043
Cis-1,2-dichloroethene	524.2		0.040	0.033	-0.010	0.203

Table 2. Comparison of Detection Limits (µg/L except where footnoted) for the Episode 6000 Data set

Analyte	Method	Procedure	EPA/ ACS DL	ISO CRV	ISO MDV	ASTM SL-IDE
Cis-1,3-dichloropropene	502.2	ELCD	0.007	0.016	0.031	0.059
Cis-1,3-dichloropropene	502.2	PID	0.057	0.048	0.099	0.077
Cis-1,3-dichloropropene	524.2		0.038	0.024	0.001	0.158
Cobalt	1620		9.820	4.017	8.094	15.560
Cobalt	200.8		0.001	0.001	-0.070	0.008
Copper	1620		6.046	4.990	10.510	20.328
Copper	200.8		0.037	0.027	0.053	0.770
Dibromochloromethane	502.2	ELCD	0.009	0.019	0.039	0.418
Dibromochloromethane	524.2		0.051	0.031	0.011	0.253
Dibromomethane	502.2	ELCD	0.007	0.047	0.096	0.441
Dibromomethane	524.2		0.102	0.082	0.117	0.342
Dichlorodifluoromethane	502.2	ELCD	0.009	1.453	1.715	0.087
Dichlorodifluoromethane	524.2		0.083	0.054	0.046	0.420
Diethyl Ether	524.2		0.120	0.114	0.169	0.340
Ethyl Methacrylate	524.2		0.045	0.031	0.018	0.244
Ethylbenzene	502.2	PID	0.021	0.053	0.122	0.075
Ethylbenzene	524.2		0.033	0.028	-0.020	0.167
Hardness [1]	130.2		0.828	0.555	1.152	2.152
Hexachlorobutadiene	502.2	ELCD	0.043	0.240	0.502	0.090
Hexachlorobutadiene	524.2		0.068	0.035	-0.020	0.263
Hexachloroethane	524.2		0.056	0.049	0.044	0.234
Hexchlobutadiene+naphthalene	502.2	PID	0.649	0.924	2.083	0.598
Iron	1620		90.409	270.433	472.200	345.686
Isopropylbenzene	502.2	PID	0.020	0.051	0.120	0.059
Isopropylbenzene	524.2		0.011	0.010	0.012	0.113
Lead	1620		1.647	1.186	1.965	2.317
Lead	200.8		0.655	0.061	0.120	0.197
M+p Xylene	502.2	PID	0.090	0.099	0.225	0.116
M+p Xylene	524.2		0.013	0.008	0.006	0.127
Magnesium	1620		103.033	88.729	175.300	99.662
Manganese	1620		6.856	1.081	2.591	6.531
Manganese	200.8		0.031	0.030	0.049	0.106
Mercury	200.8		0.004	0.003	-0.020	0.062
Methacrylonitrile	524.2		0.356	0.228	0.368	0.643

Table 2. Comparison of Detection Limits (µg/L except where footnoted) for the Episode 6000 Data set

Analyte	Method	Procedure	EPA/ ACS DL	ISO CRV	ISO MDV	ASTM SL-IDE
Methyl Iodide	524.2		0.025	0.023	-0.010	0.173
Methyl Tert-butyl Ether	524.2		0.026	0.016	-0.030	0.195
Methylacrylate	524.2		0.220	0.202	0.356	0.549
Methylene Chloride	502.2	ELCD	0.128	1.835	5.018	2.727
Methylene Chloride	524.2		0.082	0.072	0.098	0.276
Methylmethacrylate	524.2		0.225	0.085	0.120	0.484
Molybdenum	1620		2.455	1.714	3.787	2.917
Molybdenum	200.8		0.004	0.003	0.000	0.262
N-butylbenzene	502.2	PID	0.030	0.069	0.151	0.139
N-butylbenzene	524.2		0.016	0.014	0.027	0.136
N-propylbenzene	502.2	PID	0.040	0.597	1.340	0.089
N-propylbenzene	524.2		0.038	0.026	-0.040	0.231
Naphthalene	524.2		0.048	0.040	0.047	0.175
Nickel	1620		20.219	13.262	25.700	23.784
Nickel	200.8		0.146	0.058	0.107	0.076
o-xylene	524.2		0.018	0.015	-0.030	0.161
o-xylene+styrene	502.2	PID	0.059	0.118	0.263	0.111
P-isoproptol+1,4-dcb	502.2	PID	0.073	0.152	0.332	0.153
Pentachloroethane	524.2		0.553	0.019	-0.080	0.337
Sec-butylbenzene	502.2	PID	0.055	0.058	0.133	0.079
Sec-butylbenzene	524.2		0.014	0.011	-0.010	0.132
Selenium	1620		0.849	0.619	1.493	1.915
Selenium	200.8		0.192	0.156	0.302	0.410
Silver	1620		4.907	3.588	6.495	10.219
Silver	200.8		0.004	0.002	0.004	0.010
Sodium	1620		69.530	49.595	97.650	133.007
Styrene	524.2		0.014	0.011	0.011	0.119
Tert-butylbenzene	502.2	PID	0.029	0.058	0.137	0.073
Tert-butylbenzene	524.2		0.022	0.012	0.023	0.170
Tetrachloroethene	502.2	ELCD	0.018	0.200	0.429	0.051
Tetrachloroethene	502.2	PID	0.062	0.319	0.753	0.157
Tetrachloroethene	524.2		0.085	0.084	0.058	0.379
Thallium	1620		0.512	0.651	1.406	1.208
Thallium	200.8		0.000	0.000	0.001	0.001

Table 2. Comparison of Detection Limits (µg/L except where footnoted) for the Episode 6000 Data set

Analyte	Method	Procedure	EPA/ ACS DL	ISO CRV	ISO MDV	ASTM SL-IDE
Thorium	200.8		0.001	0.001	0.000	0.003
Tin	1620		3.670	2.019	3.143	1.200
Titanium	1620		4.777	4.453	8.050	5.238
Toluene	502.2	PID	0.070	0.064	0.145	0.061
Toluene	524.2		0.020	0.006	0.000	0.130
Total Phosphorus [1]	365.2		0.006	0.005	0.009	0.013
Total Suspended Solids [1]	160.2		1.170	0.948	1.945	2.877
Trans-1,2-dichloroethene	502.2	ELCD	0.041	0.174	0.382	0.065
Trans-1,2-dichloroethene	524.2		0.038	0.032	-0.010	0.255
Trans-1,3-dichloropropene	502.2	ELCD	0.012	0.013	0.026	0.082
Trans-1,3-dichloropropene	502.2	PID	0.058	0.037	0.079	0.085
Trans-1,3-dichloropropene	524.2		0.051	0.025	0.000	0.204
Trans-1,4-dichloro-2-butene	524.2		0.512	0.348	0.589	1.182
Trichloroethene	502.2	ELCD	0.012	0.014	0.029	0.050
Trichloroethene	502.2	PID	0.027	0.043	0.098	0.096
Trichloroethene	524.2		0.061	0.058	0.062	0.288
Trichlorofluoromethane	502.2	ELCD	0.108	0.012	0.028	1.997
Trichlorofluoromethane	524.2		0.087	0.075	0.046	0.307
Uranium	200.8		0.000	0.000	0.000	0.001
Vanadium	1620		7.344	4.207	8.359	10.063
Vanadium	200.8		0.555	0.512	0.994	0.845
Vinyl Chloride	502.2	ELCD	0.270	0.039	0.072	3.521
Vinyl Chloride	524.2		0.043	0.031	0.000	0.295
WAD Cyanide	1677		0.572	0.169	0.319	0.672
Xylene (Total)	524.2		0.009	0.005	0.008	0.111
Yttrium	1620		1.923	1.370	2.518	3.119
Zinc	1620		2.597	2.301	3.697	4.415
Zinc	200.8		0.900	0.461	0.806	1.497

[1] Results reported as mg/L

Note: ELCD or PID in the Procedure column indicates the photo-ionization detector (PID) or electrolytic conductivity detector (ELCD) in EPA Method 502.2

Table 3. Ratios ofDetection Limits to the EPA/ACS DL for the Episode 6000 Data Set

Analyte	Method	Procedure	ISO CRV/ MDL	ISO MDV/ MDL	SL-IDE/ MDL
1,1,1,2-tetrachloroethane	502.2	ELCD	0.691	1.313	0.679
1,1,1,2-tetrachloroethane	524.2		0.747	-0.645	3.953
1,1,1-trichloroethane	502.2	ELCD	0.707	1.387	2.861
1,1,1-trichloroethane	524.2		0.382	0.135	4.843
1,1,2,2-tce+1,2,3-tcp	502.2	ELCD	3.522	6.531	2.664
1,1,2,2-tetrachloroethane	524.2		0.994	1.054	2.853
1,1,2-trichloroethane	502.2	ELCD	2.266	4.207	1.062
1,1,2-trichloroethane	524.2		0.580	0.602	3.796
1,1-dichloroethane	502.2	ELCD	0.786	1.645	6.600
1,1-dichloroethane	524.2		0.596	0.561	6.281
1,1-dichloroethene	502.2	ELCD	0.348	0.845	5.018
1,1-dichloroethene	524.2		0.647	-0.477	5.102
1,1-dichloropropanone	524.2		0.607	1.091	1.164
1,1-dichloropropene	524.2		0.261	-0.536	5.525
1,2,3-trichlorobenzene	502.2	ELCD	6.454	12.543	2.548
1,2,3-trichlorobenzene	502.2	PID	5.268	10.902	1.988
1,2,3-trichlorobenzene	524.2		0.578	0.517	3.706
1,2,3-trichloropropane	524.2		0.006	0.006	0.165
1,2,4-trichlorobenzene	502.2	ELCD	8.731	18.213	3.548
1,2,4-trichlorobenzene	502.2	PID	3.143	6.704	1.773
1,2,4-trichlorobenzene	524.2		0.951	1.069	3.921
1,2,4-trimethylbenzene	502.2	PID	0.792	1.766	1.297
1,2,4-trimethylbenzene	524.2		0.772	1.419	10.509
1,2-dibromo-3-chloropropane	524.2		0.268	0.482	1.111
1,2-dibromoethane	502.2	ELCD	0.297	0.582	1.496
1,2-dibromoethane	524.2		0.918	1.378	2.275
1,2-dichlorobenzene	502.2	ELCD	2.079	4.106	1.525
1,2-dichlorobenzene	502.2	PID	0.734	1.649	4.514
1,2-dichlorobenzene	524.2		0.755	-0.319	3.729
1,2-dichloroethane	502.2	ELCD	0.981	1.834	2.107
1,2-dichloroethane	524.2		0.609	0.445	5.882
1,2-dichloropropane	502.2	ELCD	8.543	17.176	1.602
1,2-dichloropropane	524.2		0.540	0.519	3.915
1,3,5-tmb+4-chlorotoluene	502.2	PID	2.984	6.658	1.598

Table 3. Ratios ofDetection Limits to the EPA/ACS DL for the Episode 6000 Data Set

Analyte	Method	Procedure	ISO CRV/ MDL	ISO MDV/ MDL	SL-IDE/ MDL
1,3,5-trimethylbenzene	524.2		0.710	0.843	10.494
1,3-dichlorobenzene	502.2	ELCD	1.375	2.980	2.850
1,3-dichlorobenzene	502.2	PID	1.445	3.192	1.325
1,3-dichlorobenzene	524.2		0.699	-0.357	5.418
1,3-dichloropropane	502.2	ELCD	4.518	8.588	2.839
1,3-dichloropropane	524.2		0.628	-0.212	4.457
1,4-dichlorobenzene	502.2	ELCD	3.876	7.630	2.068
1,4-dichlorobenzene	524.2		0.714	-1.534	4.699
1-chlorobutane	524.2		0.786	0.974	10.051
2,2-dichloropropane	524.2		0.044	-0.049	0.294
2-butanone	524.2		0.713	1.235	1.860
2-chlorotoluene	502.2	ELCD	1.498	2.947	1.705
2-chlorotoluene	502.2	PID	1.907	4.290	0.931
2-chlorotoluene	524.2		0.570	0.215	7.599
2-hexanone	524.2		0.112	0.178	0.620
2-nitropropane	524.2		0.305	0.507	1.071
4-chlorotoluene	502.2	ELCD	1.152	2.135	1.445
4-chlorotoluene	524.2		0.803	0.849	10.563
4-isopropyltoluene	524.2		0.833	0.519	10.452
4-methyl-2-pentanone	524.2		0.591	0.911	1.305
Acetone	524.2		0.512	0.938	2.358
Acrylonitrile	524.2		0.515	0.763	1.387
Allyl Chloride	524.2		0.820	0.306	6.297
Aluminum	1620		0.509	0.970	6.718
Aluminum	200.8		0.088	0.185	0.627
Ammonia as Nitrogen	350.3		0.668	1.358	1.229
Antimony	1620		0.516	1.130	2.634
Antimony	200.8		0.018	0.037	0.102
Arsenic	1620		0.861	1.290	1.373
Arsenic	200.8		0.606	1.206	1.532
Barium	1620		0.786	1.076	1.035
Barium	200.8		0.885	1.855	2.421
Benzene	502.2	PID	1.435	3.283	2.537
Benzene	524.2		0.981	1.839	7.986

Table 3. Ratios ofDetection Limits to the EPA/ACS DL for the Episode 6000 Data Set

Analyte	Method	Procedure	ISO CRV/ MDL	ISO MDV/ MDL	SL-IDE/ MDL
Beryllium	1620		0.641	0.773	0.810
Beryllium	200.8		0.564	0.846	2.667
Boron	1620		0.673	1.156	1.292
Bromobenzene	502.2	ELCD	0.711	1.428	5.575
Bromobenzene	502.2	PID	23.364	50.631	3.947
Bromobenzene	524.2		0.834	-1.041	4.021
Bromochloromethane	502.2	ELCD	1.166	2.381	34.635
Bromochloromethane	524.2		0.902	1.319	2.468
Bromodichloromethane	502.2	ELCD	3.804	7.753	15.209
Bromodichloromethane	524.2		0.614	0.538	4.229
Bromoform	502.2	ELCD	1.503	2.627	242.497
Bromoform	524.2		0.523	0.323	2.835
Bromomethane	502.2	ELCD	0.178	0.037	26.202
Bromomethane	524.2		0.810	0.893	3.516
Cadmium	1620		0.619	1.056	1.449
Cadmium	200.8		1.769	2.985	2.793
Calcium	1620		0.975	1.971	1.080
Carbon Disulfide	524.2		0.582	-1.199	7.610
Carbon Tetrachloride	524.2		0.711	-0.770	6.751
Carbontet+1,1-dcp	502.2	ELCD	0.986	2.089	2.162
Chloroacetonitrile	524.2		0.841	1.671	1.671
Chlorobenzene	502.2	ELCD	1.373	2.964	38.584
Chlorobenzene	502.2	PID	2.654	5.904	2.063
Chlorobenzene	524.2		0.880	0.643	4.864
Chloroethane	502.2	ELCD	0.051	0.041	23.132
Chloroethane	524.2		0.619	0.637	5.069
Chloroform	502.2	ELCD	9.595	17.716	0.722
Chloroform	524.2		0.745	0.692	5.610
Chloromethane	502.2	ELCD	1.292	3.452	2.934
Chloromethane	524.2		0.803	1.469	4.798
Chromium	1620		0.819	1.246	1.545
Chromium	200.8		0.847	1.713	5.391
Cis-1,2-dce+2,2-dcp	502.2	ELCD	1.334	2.619	3.344
Cis-1,2-dichloroethene	524.2		0.826	-0.342	5.104

Table 3. Ratios ofDetection Limits to the EPA/ACS DL for the Episode 6000 Data Set

Analyte	Method	Procedure	ISO CRV/ MDL	ISO MDV/ MDL	SL-IDE/ MDL
Cis-1,3-dichloropropene	502.2	ELCD	2.183	4.379	8.267
Cis-1,3-dichloropropene	502.2	PID	0.839	1.742	1.367
Cis-1,3-dichloropropene	524.2		0.616	0.038	4.116
Cobalt	1620		0.409	0.824	1.585
Cobalt	200.8		0.790	-64.641	8.058
Copper	1620		0.825	1.739	3.362
Copper	200.8		0.716	1.429	20.667
Dibromochloromethane	502.2	ELCD	2.077	4.211	45.610
Dibromochloromethane	524.2		0.600	0.208	4.953
Dibromomethane	502.2	ELCD	7.153	14.604	67.146
Dibromomethane	524.2		0.806	1.145	3.356
Dichlorodifluoromethane	502.2	ELCD	163.453	192.935	9.771
Dichlorodifluoromethane	524.2		0.651	0.551	5.027
Diethyl Ether	524.2		0.952	1.412	2.837
Ethyl Methacrylate	524.2		0.681	0.401	5.391
Ethylbenzene	502.2	PID	2.459	5.663	3.496
Ethylbenzene	524.2		0.833	-0.475	4.992
Hardness	130.2		0.669	1.391	2.598
Hexachlorobutadiene	502.2	ELCD	5.586	11.673	2.097
Hexachlorobutadiene	524.2		0.519	-0.293	3.866
Hexachloroethane	524.2		0.883	0.782	4.186
Hexchlobutadiene+naphthalene	502.2	PID	1.423	3.208	0.920
Iron	1620		2.991	5.223	3.824
Isopropylbenzene	502.2	PID	2.530	5.930	2.921
Isopropylbenzene	524.2		0.920	1.099	10.555
Lead	1620		0.720	1.193	1.407
Lead	200.8		0.093	0.183	0.301
M+p Xylene	502.2	PID	1.093	2.496	1.281
M+p Xylene	524.2		0.588	0.449	9.870
Magnesium	1620		0.861	1.702	0.967
Manganese	1620		0.158	0.378	0.953
Manganese	200.8		0.974	1.587	3.450
Mercury	200.8		0.799	-4.048	14.165
Methacrylonitrile	524.2		0.642	1.034	1.808

Table 3. Ratios ofDetection Limits to the EPA/ACS DL for the Episode 6000 Data Set

Analyte	Method	Procedure	ISO CRV/ MDL	ISO MDV/ MDL	SL-IDE/ MDL
Methyl Iodide	524.2		0.924	-0.257	6.826
Methyl Tert-butyl Ether	524.2		0.630	-1.011	7.514
Methylacrylate	524.2		0.918	1.618	2.495
Methylene Chloride	502.2	ELCD	14.312	39.130	21.261
Methylene Chloride	524.2		0.875	1.196	3.367
Methylmethacrylate	524.2		0.376	0.535	2.153
Molybdenum	1620		0.698	1.543	1.188
Molybdenum	200.8		0.777	0.013	68.949
N-butylbenzene	502.2	PID	2.322	5.050	4.676
N-butylbenzene	524.2		0.890	1.694	8.614
N-propylbenzene	502.2	PID	14.846	33.306	2.221
N-propylbenzene	524.2		0.676	-1.102	6.104
Naphthalene	524.2		0.821	0.983	3.622
Nickel	1620		0.656	1.271	1.176
Nickel	200.8		0.397	0.736	0.524
o-xylene	524.2		0.802	-1.396	8.734
o-xylene+styrene	502.2	PID	2.012	4.469	1.893
P-isoproptol+1,4-dcb	502.2	PID	2.090	4.573	2.107
Pentachloroethane	524.2		0.035	-0.153	0.610
Sec-butylbenzene	502.2	PID	1.039	2.402	1.429
Sec-butylbenzene	524.2		0.762	-0.517	9.507
Selenium	1620		0.729	1.759	2.256
Selenium	200.8		0.815	1.577	2.139
Silver	1620		0.731	1.324	2.082
Silver	200.8		0.441	0.947	2.581
Sodium	1620		0.713	1.404	1.913
Styrene	524.2		0.797	0.815	8.467
Tert-butylbenzene	502.2	PID	2.024	4.819	2.575
Tert-butylbenzene	524.2		0.535	1.065	7.707
Tetrachloroethene	502.2	ELCD	11.204	23.979	2.831
Tetrachloroethene	502.2	PID	5.175	12.216	2.540
Tetrachloroethene	524.2		0.997	0.688	4.482
Thallium	1620		1.273	2.747	2.361
Thallium	200.8		1.038	1.964	3.125

Table 3. Ratios ofDetection Limits to the EPA/ACS DL for the Episode 6000 Data Set

Analyte	Method	Procedure	ISO CRV/ MDL	ISO MDV/ MDL	SL-IDE/ MDL
Thorium	200.8		0.836	-6.702	4.345
Tin	1620		0.550	0.856	0.327
Titanium	1620		0.932	1.685	1.097
Toluene	502.2	PID	0.923	2.068	0.873
Toluene	524.2		0.280	-0.100	6.591
Total Phosphorus	365.2		0.777	1.572	2.202
Total Suspended Solids	160.2		0.810	1.662	2.459
Trans-1,2-dichloroethene	502.2	ELCD	4.267	9.382	1.603
Trans-1,2-dichloroethene	524.2		0.834	-0.210	6.695
Trans-1,3-dichloropropene	502.2	ELCD	1.098	2.183	6.938
Trans-1,3-dichloropropene	502.2	PID	0.641	1.358	1.454
Trans-1,3-dichloropropene	524.2		0.486	-0.008	4.018
Trans-1,4-dichloro-2-butene	524.2		0.680	1.150	2.310
Trichloroethene	502.2	ELCD	1.157	2.435	4.169
Trichloroethene	502.2	PID	1.592	3.635	3.539
Trichloroethene	524.2		0.952	1.009	4.690
Trichlorofluoromethane	502.2	ELCD	0.114	0.256	18.504
Trichlorofluoromethane	524.2		0.858	0.527	3.516
Uranium	200.8		0.495	0.757	2.519
Vanadium	1620		0.573	1.138	1.370
Vanadium	200.8		0.923	1.791	1.522
Vinyl Chloride	502.2	ELCD	0.144	0.268	13.063
Vinyl Chloride	524.2		0.719	0.004	6.845
WAD Cyanide	1677		0.296	0.558	1.175
Xylene (Total)	524.2		0.575	0.850	12.430
Yttrium	1620		0.712	1.310	1.622
Zinc	1620		0.886	1.423	1.700
Zinc	200.8		0.511	0.895	1.663

Note: ELCD or PID in the Procedure column indicates the photo-ionization detector (PID) or electrolytic conductivity detector (ELCD) in EPA Method 502.2

Summary Statistics for Table 3

	ISO CRV/ EPA/ACS DL	ISO MDV/ EPA/ACS DL	SL-IDE/ EPA/ACS DL
Minimum	0.01	-64.64	0.10
25th percentile	0.61	0.52	1.60
Median	0.80	1.17	2.86
75th percentile	1.08	2.17	5.41
Maximum	163.45	192.93	242.50
	Number of analytes	**Percent of analytes**	**p-value for percent=50**
CRV>DL	52	26.26%	<0.0001
MDV>DL	113	57.07%	0.055
SL-IDE>DL	181	91.41%	<0.0001

Table 4. Comparison Quantitation Limits for the Episode 6000 Data Set (µg/L except where footnoted)

Analyte	Method	Procedure	EPA/ ACS QL	ISO/ IUPAC LOQ	ASTM SL-IQE
1,1,1,2-tetrachloroethane	502.2	ELCD	0.2	0.152	0.030
1,1,1,2-tetrachloroethane	524.2		0.2	0.183	0.181
1,1,1-trichloroethane	502.2	ELCD	0.1	0.044	0.830
1,1,1-trichloroethane	524.2		0.5	0.102	0.240
1,1,2,2-tce+1,2,3-tcp	502.2	ELCD	0.5	1.110	5.514
1,1,2,2-tetrachloroethane	524.2		0.5	0.596	0.569
1,1,2-trichloroethane	502.2	ELCD	0.1	0.289	0.060
1,1,2-trichloroethane	524.2		0.5	0.212	0.290
1,1-dichloroethane	502.2	ELCD	0.05	0.047	0.527
1,1-dichloroethane	524.2		0.2	0.099	0.115
1,1-dichloroethene	502.2	ELCD	0.1	0.096	3.796
1,1-dichloroethene	524.2		0.2	0.159	0.129
1,1-dichloropropanone	524.2		20	15.396	12.705
1,1-dichloropropene	524.2		0.5	0.057	0.180
1,2,3-trichlorobenzene	502.2	ELCD	0.2	1.750	0.851
1,2,3-trichlorobenzene	502.2	PID	0.2	1.818	0.248
1,2,3-trichlorobenzene	524.2		0.2	0.192	0.216
1,2,3-trichloropropane	524.2		20	0.267	11.316

Table 4. Comparison Quantitation Limits for the Episode 6000 Data Set (µg/L except where footnoted)

Analyte	Method	Procedure	EPA/ ACS QL	ISO/ IUPAC LOQ	ASTM SL-IQE
1,2,4-trichlorobenzene	502.2	ELCD	0.1	1.150	0.401
1,2,4-trichlorobenzene	502.2	PID	0.2	1.371	0.439
1,2,4-trichlorobenzene	524.2		0.2	0.231	0.141
1,2,4-trimethylbenzene	502.2	PID	0.5	0.485	0.653
1,2,4-trimethylbenzene	524.2		0.1	0.050	20.896
1,2-dibromo-3-chloropropane	524.2		10	1.843	71.182
1,2-dibromoethane	502.2	ELCD	0.5	0.156	0.592
1,2-dibromoethane	524.2		0.5	0.560	0.417
1,2-dichlorobenzene	502.2	ELCD	0.1	0.418	0.183
1,2-dichlorobenzene	502.2	PID	0.1	0.139	0.346
1,2-dichlorobenzene	524.2		0.1	0.101	0.085
1,2-dichloroethane	502.2	ELCD	0.1	0.089	0.065
1,2-dichloroethane	524.2		0.5	0.122	0.222
1,2-dichloropropane	502.2	ELCD	0.1	1.138	0.102
1,2-dichloropropane	524.2		0.5	0.148	0.196
1,3,5-tmb+4-chlorotoluene	502.2	PID	0.2	1.275	0.189
1,3,5-trimethylbenzene	524.2		0.1	0.044	23.744
1,3-dichlorobenzene	502.2	ELCD	0.1	0.301	0.936
1,3-dichlorobenzene	502.2	PID	0.2	0.840	0.465
1,3-dichlorobenzene	524.2		0.1	0.080	0.076
1,3-dichloropropane	502.2	ELCD	0.1	0.356	0.054
1,3-dichloropropane	524.2		0.2	0.114	0.139
1,4-dichlorobenzene	502.2	ELCD	0.1	0.571	0.101
1,4-dichlorobenzene	524.2		0.1	0.069	0.078
1-chlorobutane	524.2		0.1	0.082	29.943
2,2-dichloropropane	524.2		10	0.568	38.009
2-butanone	524.2		2	1.416	0.893
2-chlorotoluene	502.2	ELCD	0.5	0.881	0.493
2-chlorotoluene	502.2	PID	1	2.877	0.849
2-chlorotoluene	524.2		0.1	0.046	0.053
2-hexanone	524.2		10	0.669	0.442
2-nitropropane	524.2		10	1.280	0.590
4-chlorotoluene	502.2	ELCD	0.5	0.668	0.142 [1]
4-chlorotoluene	524.2		0.1	0.037	23.810

Table 4. Comparison Quantitation Limits for the Episode 6000 Data Set (µg/L except where footnoted)

Analyte	Method	Procedure	EPA/ ACS QL	ISO/ IUPAC LOQ	ASTM SL-IQE
4-isopropyltoluene	524.2		0.1	0.043	0.016
4-methyl-2-pentanone	524.2		5	2.065	1.785
Acetone	524.2		2	2.115	2.741
Acrylonitrile	524.2		5	1.816	28.056
Allyl Chloride	524.2		0.2	0.129	29.674
Aluminum	1620		100	76.242	464.069
Aluminum	200.8		50	9.418	29.684
Ammonia as Nitrogen [2]	350.3		0.05	0.037	0.035
Antimony	1620		5	4.784	9.551
Antimony	200.8		0.5	0.017	0.034
Arsenic	1620		5	3.684	3.097
Arsenic	200.8		1	0.720	0.798
Barium	1620		5	4.722	4.118
Barium	200.8		0.1	0.161	0.211
Benzene	502.2	PID	0.1	0.273	0.182
Benzene	524.2		0.05	0.075	0.044
Beryllium	1620		2	1.055	0.980
Beryllium	200.8		0.02	0.018	0.044
Boron	1620		100	46.040	51.134
Bromobenzene	502.2	ELCD	0.5	0.593	3.529
Bromobenzene	502.2	PID	0.05	1.767	0.100
Bromobenzene	524.2		0.2	0.167	0.140
Bromochloromethane	502.2	ELCD	0.1	0.090	1.598
Bromochloromethane	524.2		0.5	0.549	0.368
Bromodichloromethane	502.2	ELCD	0.05	0.091	0.424
Bromodichloromethane	524.2		0.2	0.135	0.128
Bromoform	502.2	ELCD	0.2	0.056	3.393
Bromoform	524.2		0.5	0.287	0.482
Bromomethane	502.2	ELCD	1	undefined [3]	16.351
Bromomethane	524.2		0.2	0.252	0.226
Cadmium	1620		0.5	0.346	0.410
Cadmium	200.8		0.02	0.046	0.063
Calcium	1620		100	186.530	99.975
Carbon Disulfide	524.2		0.1	0.077	0.101

Table 4. Comparison Quantitation Limits for the Episode 6000 Data Set (µg/L except where footnoted)

Analyte	Method	Procedure	EPA/ ACS QL	ISO/ IUPAC LOQ	ASTM SL-IQE
Carbon Tetrachloride	524.2		0.2	0.127	0.140
Carbontet+1,1-dcp	502.2	ELCD	0.2	0.173	0.069
Chloroacetonitrile	524.2		10	4.169	3.310
Chlorobenzene	502.2	ELCD	0.1	0.092	1.766
Chlorobenzene	502.2	PID	0.1	0.504	0.119
Chlorobenzene	524.2		0.1	0.108	0.059
Chloroethane	502.2	ELCD	0.5	0.037	5.826
Chloroethane	524.2		0.5	0.185	0.255
Chloroform	502.2	ELCD	0.2	2.217	0.025
Chloroform	524.2		0.2	0.138	0.121
Chloromethane	502.2	ELCD	0.2	0.709	1.734
Chloromethane	524.2		0.2	0.181	0.141
Chromium	1620		1	0.993	1.259
Chromium	200.8		0.2	0.331	1.028
Cis-1,2-dce+2,2-dcp	502.2	ELCD	0.05	0.097	0.039
Cis-1,2-dichloroethene	524.2		0.5	0.154	0.144
Cis-1,3-dichloropropene	502.2	ELCD	0.1	0.090	0.415
Cis-1,3-dichloropropene	502.2	PID	0.2	0.254	0.017 [1]
Cis-1,3-dichloropropene	524.2		0.2	0.116	0.141
Cobalt	1620		50	20.916	40.837
Cobalt	200.8		0.005	undefined [3]	undefined [4]
Copper	1620		20	27.513	47.509
Copper	200.8		0.1	0.142	1.825
Dibromochloromethane	502.2	ELCD	0.1	0.106	1.252
Dibromochloromethane	524.2		0.5	0.149	0.288
Dibromomethane	502.2	ELCD	0.1	0.257	1.395
Dibromomethane	524.2		0.5	0.400	0.460
Dichlorodifluoromethane	502.2	ELCD	0.1	5.759	1.091
Dichlorodifluoromethane	524.2		0.5	0.289	0.480
Diethyl Ether	524.2		0.5	0.563	0.404
Ethyl Methacrylate	524.2		0.5	0.139	0.183
Ethylbenzene	502.2	PID	0.1	0.341	0.157
Ethylbenzene	524.2		0.2	0.123	0.077
Hardness [2]	130.2		2	2.973	5.465

Table 4. Comparison Quantitation Limits for the Episode 6000 Data Set (µg/L except where footnoted)

Analyte	Method	Procedure	EPA/ ACS QL	ISO/ IUPAC LOQ	ASTM SL-IQE
Hexachlorobutadiene	502.2	ELCD	0.2	1.466	0.243
Hexachlorobutadiene	524.2		0.2	0.160	0.228
Hexachloroethane	524.2		0.2	0.232	0.167
Hexchlobutadiene+naphthalene	502.2	PID	2	6.108	1.542
Iron	1620		200	1490.589	996.565
Isopropylbenzene	502.2	PID	0.1	0.337	0.129
Isopropylbenzene	524.2		0.1	0.056	25.592
Lead	1620		5	5.062	5.698
Lead	200.8		2	0.318	0.685
M+p Xylene	502.2	PID	0.2	0.652	0.222
M+p Xylene	524.2		0.1	0.042	24.651
Magnesium	1620		500	454.043	267.199
Manganese	1620		20	7.948	15.264
Manganese	200.8		0.1	0.133	0.245
Mercury	200.8		0.02	0.056	0.039
Methacrylonitrile	524.2		2	1.065	19.062
Methyl Iodide	524.2		0.2	0.108	0.083
Methyl Tert-butyl Ether	524.2		0.5	0.073	0.122
Methylacrylate	524.2		1	0.966	0.727
Methylene Chloride	502.2	ELCD	1	undefined [3]	6.033
Methylene Chloride	524.2		0.2	0.354	0.433
Methylmethacrylate	524.2		1	0.381	20.773
Molybdenum	1620		10	9.752	7.597
Molybdenum	200.8		0.01	0.052	0.608
N-butylbenzene	502.2	PID	0.1	0.429	0.745
N-butylbenzene	524.2		0.1	0.077	0.067
N-propylbenzene	502.2	PID	0.2	3.869	0.186
N-propylbenzene	524.2		0.2	0.110	29.878
Naphthalene	524.2		0.2	0.184	0.108
Nickel	1620		100	66.486	67.206
Nickel	200.8		0.5	0.287	0.183
o-xylene	524.2		0.2	0.062	0.040
o-xylene+styrene	502.2	PID	0.2	0.746	0.181
P-isoproptol+1,4-dcb	502.2	PID	0.2	0.956	0.456

Table 4. Comparison Quantitation Limits for the Episode 6000 Data Set (µg/L except where footnoted)

Analyte	Method	Procedure	EPA/ ACS QL	ISO/ IUPAC LOQ	ASTM SL-IQE
Pentachloroethane	524.2		2	0.086	0.551
Sec-butylbenzene	502.2	PID	0.2	0.377	0.157
Sec-butylbenzene	524.2		0.1	0.063	0.047
Selenium	1620		2	3.859	5.235
Selenium	200.8		1	0.805	1.045
Silver	1620		20	16.734	25.842
Silver	200.8		0.02	0.011	0.056
Sodium	1620		200	251.546	337.755
Styrene	524.2		0.1	0.054	0.041
Tert-butylbenzene	502.2	PID	0.1	0.391	0.203
Tert-butylbenzene	524.2		0.1	0.063	0.073
Tetrachloroethene	502.2	ELCD	0.1	1.226	0.122
Tetrachloroethene	502.2	PID	0.2	2.084	0.750
Tetrachloroethene	524.2		0.2	0.377	30.554
Thallium	1620		2	3.748	2.799
Thallium	200.8		0.001	0.002	0.003
Thorium	200.8		0.002	0.005	0.004
Tin	1620		10	9.237	9.406
Titanium	1620		20	20.807	14.236
Toluene	502.2	PID	0.2	0.409	0.194
Toluene	524.2		0.2	0.028	0.046
Total Phosphorus [2]	365.2		0.02	0.024	0.030
Total Suspended Solids [2]	160.2		5	5.011	6.729
Trans-1,2-dichloroethene	502.2	ELCD	0.2	1.060	0.191
Trans-1,2-dichloroethene	524.2		0.2	0.140	0.153
Trans-1,3-dichloropropene	502.2	ELCD	0.1	0.073	0.729
Trans-1,3-dichloropropene	502.2	PID	0.2	0.205	0.175
Trans-1,3-dichloropropene	524.2		0.5	0.121	0.218
Trans-1,4-dichloro-2-butene	524.2		2	1.801	30.108
Trichloroethene	502.2	ELCD	0.1	0.081	3.169
Trichloroethene	502.2	PID	0.1	0.260	0.401
Trichloroethene	524.2		0.2	0.283	0.167
Trichlorofluoromethane	502.2	ELCD	0.5	0.085	4.662
Trichlorofluoromethane	524.2		0.5	0.279	42.490

Table 4. Comparison Quantitation Limits for the Episode 6000 Data Set (µg/L except where footnoted)

Analyte	Method	Procedure	EPA/ ACS QL	ISO/ IUPAC LOQ	ASTM SL-IQE
Uranium	200.8		0.001	0.001	0.002
Vanadium	1620		20	21.586	24.338
Vanadium	200.8		2	2.627	1.933
Vinyl Chloride	502.2	ELCD	1	0.270	8.234
Vinyl Chloride	524.2		0.2	0.139	0.219
WAD Cyanide	1677		2	0.852	1.624
Xylene (Total)	524.2		0.1	0.027	23.520
Yttrium	1620		5	6.571	8.962
Zinc	1620		10	9.575	10.452
Zinc	200.8		2	2.147	7.024

[1] IQE 10% undefined, IQE 20% reported
[2] Results reported as mg/L
[3] No LOQ could be calculated due to a square root of a negative number in the formula
[4] IQE 10%, IQE 20% and IQE 30% all negative based on chosen model (linear)
Note: ELCD or PID in the Procedure column indicates the photo-ionization detector (PID) or electrolytic conductivity detector (ELCD) in EPA Method 502.2

Table 5. Ratios of Quantitation Limits to the EPA/ACS QL for the Episode 6000 Data Set

Analyte	Method	Procedure	ISO LOQ/ML	SL-IQE/ML
1,1,1,2-tetrachloroethane	502.2	ELCD	0.759	0.152
1,1,1,2-tetrachloroethane	524.2		0.915	0.907
1,1,1-trichloroethane	502.2	ELCD	0.445	8.298
1,1,1-trichloroethane	524.2		0.203	0.479
1,1,2,2-tce+1,2,3-tcp	502.2	ELCD	2.220	11.027
1,1,2,2-tetrachloroethane	524.2		1.192	1.138
1,1,2-trichloroethane	502.2	ELCD	2.886	0.603
1,1,2-trichloroethane	524.2		0.424	0.579
1,1-dichloroethane	502.2	ELCD	0.949	10.531
1,1-dichloroethane	524.2		0.496	0.573
1,1-dichloroethene	502.2	ELCD	0.960	37.963
1,1-dichloroethene	524.2		0.795	0.644
1,1-dichloropropanone	524.2		0.770	0.635
1,1-dichloropropene	524.2		0.114	0.360
1,2,3-trichlorobenzene	502.2	ELCD	8.751	4.257

Table 5. Ratios of Quantitation Limits to the EPA/ACS QL for the Episode 6000 Data Set

Analyte	Method	Procedure	ISO LOQ/ML	SL-IQE/ML
1,2,3-trichlorobenzene	502.2	PID	9.092	1.239
1,2,3-trichlorobenzene	524.2		0.959	1.080
1,2,3-trichloropropane	524.2		0.013	0.566
1,2,4-trichlorobenzene	502.2	ELCD	11.502	4.010
1,2,4-trichlorobenzene	502.2	PID	6.853	2.197
1,2,4-trichlorobenzene	524.2		1.157	0.703
1,2,4-trimethylbenzene	502.2	PID	0.970	1.306
1,2,4-trimethylbenzene	524.2		0.503	208.956
1,2-dibromo-3-chloropropane	524.2		0.184	7.118
1,2-dibromoethane	502.2	ELCD	0.311	1.185
1,2-dibromoethane	524.2		1.119	0.834
1,2-dichlorobenzene	502.2	ELCD	4.178	1.833
1,2-dichlorobenzene	502.2	PID	1.393	3.455
1,2-dichlorobenzene	524.2		1.006	0.848
1,2-dichloroethane	502.2	ELCD	0.891	0.650
1,2-dichloroethane	524.2		0.244	0.443
1,2-dichloropropane	502.2	ELCD	11.378	1.023
1,2-dichloropropane	524.2		0.296	0.393
1,3,5-tmb+4-chlorotoluene	502.2	PID	6.373	0.946
1,3,5-trimethylbenzene	524.2		0.436	237.442
1,3-dichlorobenzene	502.2	ELCD	3.008	9.356
1,3-dichlorobenzene	502.2	PID	4.201	2.326
1,3-dichlorobenzene	524.2		0.800	0.760
1,3-dichloropropane	502.2	ELCD	3.560	0.539
1,3-dichloropropane	524.2		0.569	0.695
1,4-dichlorobenzene	502.2	ELCD	5.714	1.010
1,4-dichlorobenzene	524.2		0.686	0.784
1-chlorobutane	524.2		0.823	299.428
2,2-dichloropropane	524.2		0.057	3.801
2-butanone	524.2		0.708	0.446
2-chlorotoluene	502.2	ELCD	1.763	0.986
2-chlorotoluene	502.2	PID	2.877	0.849
2-chlorotoluene	524.2		0.463	0.533
2-hexanone	524.2		0.067	0.044
2-nitropropane	524.2		0.128	0.059

Table 5. Ratios of Quantitation Limits to the EPA/ACS QL for the Episode 6000 Data Set

Analyte	Method	Procedure	ISO LOQ/ML	SL-IQE/ML
4-chlorotoluene	502.2	ELCD	1.335	0.284
4-chlorotoluene	524.2		0.373	238.097
4-isopropyltoluene	524.2		0.428	0.163
4-methyl-2-pentanone	524.2		0.413	0.357
Acetone	524.2		1.057	1.371
Acrylonitrile	524.2		0.363	5.611
Allyl chloride	524.2		0.646	148.372
Aluminum	1620		0.762	4.641
Aluminum	200.8	ICP/MS	0.188	0.594
Ammonia as nitrogen	350.3		0.733	0.709
Antimony	1620		0.957	1.910
Antimony	200.8	ICP/MS	0.035	0.067
Arsenic	1620		0.737	0.619
Arsenic	200.8	ICP/MS	0.720	0.798
Barium	1620		0.944	0.824
Barium	200.8	ICP/MS	1.608	2.114
Benzene	502.2	PID	2.735	1.819
Benzene	524.2		1.509	0.877
Beryllium	1620		0.527	0.490
Beryllium	200.8	ICP/MS	0.905	2.201
Boron	1620		0.460	0.511
Bromobenzene	502.2	ELCD	1.186	7.058
Bromobenzene	502.2	PID	35.338	2.007
Bromobenzene	524.2		0.833	0.699
Bromochloromethane	502.2	ELCD	0.900	15.977
Bromochloromethane	524.2		1.097	0.737
Bromodichloromethane	502.2	ELCD	1.814	8.484
Bromodichloromethane	524.2		0.676	0.640
Bromoform	502.2	ELCD	0.282	16.964
Bromoform	524.2		0.573	0.964
Bromomethane	502.2	ELCD	N/A	16.351
Bromomethane	524.2		1.262	1.130
Cadmium	1620		0.692	0.820
Cadmium	200.8	ICP/MS	2.311	3.148
Calcium	1620		1.865	1.000

Table 5. Ratios of Quantitation Limits to the EPA/ACS QL for the Episode 6000 Data Set

Analyte	Method	Procedure	ISO LOQ/ML	SL-IQE/ML
Carbon disulfide	524.2		0.768	1.013
Carbon tetrachloride	524.2		0.635	0.700
Carbontet+1,1-dcp	502.2	ELCD	0.864	0.343
Chloroacetonitrile	524.2		0.417	0.331
Chlorobenzene	502.2	ELCD	0.921	17.658
Chlorobenzene	502.2	PID	5.040	1.190
Chlorobenzene	524.2		1.077	0.595
Chloroethane	502.2	ELCD	0.074	11.652
Chloroethane	524.2		0.369	0.510
Chloroform	502.2	ELCD	11.086	0.126
Chloroform	524.2		0.688	0.606
Chloromethane	502.2	ELCD	3.547	8.669
Chloromethane	524.2		0.906	0.703
Chromium	1620		0.993	1.259
Chromium	200.8	ICP/MS	1.653	5.142
Cis-1,2-dce+2,2-dcp	502.2	ELCD	1.941	0.780
Cis-1,2-dichloroethene	524.2		0.307	0.288
Cis-1,3-dichloropropene	502.2	ELCD	0.902	4.151
Cis-1,3-dichloropropene	502.2	PID	1.271	0.083
Cis-1,3-dichloropropene	524.2		0.582	0.706
Cobalt	1620		0.418	0.817
Cobalt	200.8	ICP/MS	N/A	N/A
Copper	1620		1.376	2.375
Copper	200.8	ICP/MS	1.419	18.250
Dibromochloromethane	502.2	ELCD	1.059	12.515
Dibromochloromethane	524.2		0.299	0.575
Dibromomethane	502.2	ELCD	2.572	13.949
Dibromomethane	524.2		0.800	0.920
Dichlorodifluoromethane	502.2	ELCD	57.590	10.907
Dichlorodifluoromethane	524.2		0.579	0.959
Diethyl ether	524.2		1.126	0.808
Ethyl methacrylate	524.2		0.279	0.366
Ethylbenzene	502.2	PID	3.413	1.573
Ethylbenzene	524.2		0.613	0.387
Hardness	130.2		1.487	2.733

Table 5. Ratios of Quantitation Limits to the EPA/ACS QL for the Episode 6000 Data Set

Analyte	Method	Procedure	ISO LOQ/ML	SL-IQE/ML
Hexachlorobutadiene	502.2	ELCD	7.332	1.215
Hexachlorobutadiene	524.2		0.799	1.142
Hexachloroethane	524.2		1.159	0.837
Hexchlobutadiene+naphthalene	502.2	PID	3.054	0.771
Iron	1620		7.453	4.983
Isopropylbenzene	502.2	PID	3.372	1.290
Isopropylbenzene	524.2		0.563	255.921
Lead	1620		1.012	1.140
Lead	200.8	ICP/MS	0.159	0.342
M+p xylene	502.2	PID	3.262	1.112
M+p xylene	524.2		0.419	246.513
Magnesium	1620		0.908	0.534
Manganese	1620		0.397	0.763
Manganese	200.8	ICP/MS	1.326	2.451
Mercury	200.8	ICP/MS	2.781	1.933
Methacrylonitrile	524.2		0.533	9.531
Methyl iodide	524.2		0.538	0.417
Methyl tert-butyl ether	524.2		0.146	0.245
Methylacrylate	524.2		0.966	0.727
Methylene chloride	502.2	ELCD	N/A	6.033
Methylene chloride	524.2		1.769	2.164
Methylmethacrylate	524.2		0.381	20.773
Molybdenum	1620		0.975	0.760
Molybdenum	200.8	ICP/MS	5.181	60.817
N-butylbenzene	502.2	PID	4.290	7.453
N-butylbenzene	524.2		0.767	0.673
N-propylbenzene	502.2	PID	19.343	0.931
N-propylbenzene	524.2		0.552	149.392
Naphthalene	524.2		0.921	0.541
Nickel	1620		0.665	0.672
Nickel	200.8	ICP/MS	0.574	0.365
O-xylene	524.2		0.310	0.202
O-xylene+styrene	502.2	PID	3.731	0.905
P-isoproptol+1,4-dcb	502.2	PID	4.778	2.281
Pentachloroethane	524.2		0.043	0.276

Table 5. Ratios of Quantitation Limits to the EPA/ACS QL for the Episode 6000 Data Set

Analyte	Method	Procedure	ISO LOQ/ML	SL-IQE/ML
Sec-butylbenzene	502.2	PID	1.885	0.784
Sec-butylbenzene	524.2		0.628	0.475
Selenium	1620		1.929	2.617
Selenium	200.8	ICP/MS	0.805	1.045
Silver	1620		0.837	1.292
Silver	200.8	ICP/MS	0.543	2.800
Sodium	1620		1.258	1.689
Styrene	524.2		0.536	0.407
Tert-butylbenzene	502.2	PID	3.911	2.027
Tert-butylbenzene	524.2		0.634	0.735
Tetrachloroethene	502.2	ELCD	12.264	1.217
Tetrachloroethene	502.2	PID	10.419	3.749
Tetrachloroethene	524.2		1.886	152.769
Thallium	1620		1.874	1.399
Thallium	200.8	ICP/MS	2.085	3.286
Thorium	200.8	ICP/MS	2.648	2.198
Tin	1620		0.924	0.941
Titanium	1620		1.040	0.712
Toluene	502.2	PID	2.045	0.971
Toluene	524.2		0.138	0.228
Total phosphorus	365.2		1.188	1.499
Total suspended solids	160.2		1.002	1.346
Trans-1,2-dichloroethene	502.2	ELCD	5.298	0.953
Trans-1,2-dichloroethene	524.2		0.702	0.764
Trans-1,3-dichloropropene	502.2	ELCD	0.731	7.286
Trans-1,3-dichloropropene	502.2	PID	1.023	0.874
Trans-1,3-dichloropropene	524.2		0.241	0.436
Trans-1,4-dichloro-2-butene	524.2		0.900	15.054
Trichloroethene	502.2	ELCD	0.812	31.690
Trichloroethene	502.2	PID	2.601	4.010
Trichloroethene	524.2		1.417	0.837
Trichlorofluoromethane	502.2	ELCD	0.171	9.325
Trichlorofluoromethane	524.2		0.558	84.980
Uranium	200.8	ICP/MS	0.721	1.853
Vanadium	1620		1.079	1.217

Table 5. Ratios of Quantitation Limits to the EPA/ACS QL for the Episode 6000 Data Set

Analyte	Method	Procedure	ISO LOQ/ML	SL-IQE/ML
Vanadium	200.8	ICP/MS	1.314	0.966
Vinyl chloride	502.2	ELCD	0.270	8.234
Vinyl chloride	524.2		0.697	1.097
Wad cyanide	1677	WADCN	0.426	0.812
Xylene (total)	524.2		0.266	235.197
Yttrium	1620		1.314	1.792
Zinc	1620		0.957	1.045
Zinc	200.8	ICP/MS	1.073	3.512

Note: ELCD or PID in the Procedure column indicates the photo-ionization detector (PID) or electrolytic conductivity detector (ELCD) in EPA Method 502.2

Summary Statistics for Table 5

	ISO LOQ/QL	SL-IQE/QL	
Minimum	0.013	0.044	
25th percentile	0.547	0.672	
Median	0.915	1.023	
75th percentile	1.792	3.512	
Maximum	57.590	299.428	
	Number of analytes	**Percent of analytes**	**p-value for percent=50**
LOQ>QL	84	43.08%	0.062
SL-IQE>QL	101	51.27%	0.776

Table 6. Frequency Comparisons for Lowest and Highest Detection and Quantitation Limits for the Episode 6000 Data Set

Detection limits				
Rank	**EPA/ACS DL**	**ISO CRV**	**ISO MDV**	**ASTM SL-IDE**
1 (lowest)	30.3%	49.5%	17.7%	2.5%
2	34.3%	33.3%	16.2%	16.2%
3	30.8%	17.2%	33.3%	18.7%
4 (highest)	4.5%	0%	32.8%	62.6%
Quantitation limits				
Rank	**EPA/ACS QL**	**No equivalent**	**ISO LOQ**	**ASTM SL-IQE**
1 (lowest)	50.5%	-	25.8%	22.2%
2	33.8%	-	26.8%	37.9%
3 (highest)	14.1%	-	46.0%	38.4%

Table 7. Detection and Quantitation Limits for EPA Methods 1631 and 1638 as Computed by EPA and by EPRI (ng/L)

		Detection limits			**Quantitation limits**		
			IDE computed by			**IQE computed by**	
Element[1]	**Ambient WQC[2]**	**MDL in Method**	**EPA**	**EPRI**	**ML in Method**	**EPA**	**EPRI**
Antimony	14000	9.7	140	110	20	270	270
Cadmium	370	25	150	150	100	540	380
Copper	2400	87	780	770	200	3800	3000
Lead	540	15	140	160	50	420	370
Mercury	12	0.2	0.5	0.43	0.5	0.55	1.6
Nickel	8200	330	220	130	1000	15000	330
Selenium	5000	450	760	600	1000	630	720
Silver	320	29	220	---	100	5500	---
Thallium	1700	7.9	27	20	20	87	50
Zinc	32000	140	1700	2100	500	21000	26100

[1] Mercury determined by EPA Method 1631; all others by EPA Method 1638
[2] Lowest ambient water quality criterion (WQC) in the National Toxics Rule (40 CFR 131.36)

Table 8. Comparison of Single-laboratory IDEs resulting from all model types for EPA Methods 1631 and 1638

Analyte	IDE, Based on Given Model			
	Constant	Linear	Exponential	Hybrid
Antimony	2400	-72 [1]	140	99
Cadmium	1200	120	150	140
Copper	2600	960	780	690
Lead	380	140	140	140
Mercury	8.1	0.059	0.79	0.50
Nickel	6600	-37 [1]	220	110
Selenium	4300	680	760	500
Silver	2400	670	220	undefined [2]
Thallium	220	21	27	16
Zinc	9600	1500	1700	1700

[1] Negative due to negative intercept estimate in precision model.
[2] IDE did not converge to a single value for estimated models.

Table 9. Comparison of 16-point and 5-point Single-laboratory IDEs (SL-IDEs) for the Episode 6000 Data Set

Analyte	Method	Procedure	SL-IDE (16)	SL-IDE (5)	SL-IDE(16)/ SL-IDE(5)	SL-IDE 16 Model	SL-IDE 5 Model
1,1,1,2-tetrachloroethane	502.2	ELCD	0.028	0.011	2.616	Exponential	Linear
1,1,1,2-tetrachloroethane	524.2		0.206	0.160	1.287	Exponential	Exponential
1,1,1-trichloroethane	502.2	ELCD	0.035	0.035	0.974	Exponential	Exponential
1,1,1-trichloroethane	524.2		0.268	0.033	8.033	Exponential	Hybrid
1,1,2,2-tce+1,2,3-tcp	502.2	ELCD	0.170	3.404	0.050	Exponential	Constant
1,1,2,2-tetrachloroethane	524.2		0.377	0.505	0.746	Exponential	Exponential
1,1,2-trichloroethane	502.2	ELCD	0.026	0.012	2.158	Exponential	Linear
1,1,2-trichloroethane	524.2		0.284	0.218	1.300	Exponential	Exponential
1,1-dichloroethane	502.2	ELCD	0.066	0.022	2.971	Exponential	Exponential
1,1-dichloroethane	524.2		0.206	0.089	2.310	Exponential	Exponential
1,1-dichloroethene	502.2	ELCD	0.193	0.068	2.834	Exponential	Exponential
1,1-dichloroethene	524.2		0.278	0.077	3.607	Exponential	Hybrid
1,1-dichloropropanone	524.2		6.032	8.566	0.704	Exponential	Exponential
1,1-dichloropropene	524.2		0.247	0.038	6.493	Exponential	Constant [1]
1,2,3-trichlorobenzene	502.2	ELCD	0.122	0.161	0.755	Exponential	Constant

Table 9. Comparison of 16-point and 5-point Single-laboratory IDEs (SL-IDEs) for the Episode 6000 Data Set							
Analyte	**Method**	**Procedure**	**SL-IDE (16)**	**SL-IDE (5)**	**SL-IDE(16)/ SL-IDE(5)**	**SL-IDE 16 Model**	**SL-IDE 5 Model**
1,2,3-trichlorobenzene	502.2	PID	0.114	0.060	1.891	Exponential	Exponential
1,2,3-trichlorobenzene	524.2		0.259	0.139	1.854	Exponential	Exponential
1,2,3-trichloropropane	524.2		1.206	0.230	5.241	Exponential	Constant [1]
1,2,4-trichlorobenzene	502.2	ELCD	0.077	0.096	0.798	Exponential	Constant
1,2,4-trichlorobenzene	502.2	PID	0.124	0.070	1.774	Exponential	Exponential
1,2,4-trichlorobenzene	524.2		0.208	0.108	1.916	Exponential	Exponential
1,2,4-trimethylbenzene	502.2	PID	0.123	0.137	0.897	Exponential	Constant
1,2,4-trimethylbenzene	524.2		0.129	0.054	2.380	Exponential	Exponential
1,2-dibromo-3-chloropropane	524.2		1.619	0.414	3.912	Exponential	Hybrid
1,2-dibromoethane	502.2	ELCD	0.143	0.023	6.138	Exponential	Linear
1,2-dibromoethane	524.2		0.289	0.302	0.958	Exponential	Exponential
1,2-dichlorobenzene	502.2	ELCD	0.053	0.053	1.007	Exponential	Linear
1,2-dichlorobenzene	502.2	PID	0.147	0.067	2.197	Exponential	Exponential
1,2-dichlorobenzene	524.2		0.112	0.065	1.727	Exponential	Exponential
1,2-dichloroethane	502.2	ELCD	0.037	0.018	2.054	Exponential	Exponential
1,2-dichloroethane	524.2		0.229	0.201	1.139	Exponential	Exponential
1,2-dichloropropane	502.2	ELCD	0.037	0.083	0.440	Exponential	Constant
1,2-dichloropropane	524.2		0.221	0.206	1.072	Exponential	Exponential
1,3,5-tmb+4-chlorotoluene	502.2	PID	0.108	0.135	0.797	Exponential	Constant
1,3,5-trimethylbenzene	524.2		0.117	0.045	2.612	Exponential	Exponential
1,3-dichlorobenzene	502.2	ELCD	0.100	0.590	0.169	Exponential	Constant
1,3-dichlorobenzene	502.2	PID	0.123	0.189	0.654	Exponential	Constant
1,3-dichlorobenzene	524.2		0.126	0.040	3.123	Exponential	Exponential
1,3-dichloropropane	502.2	ELCD	0.045	0.218	0.204	Exponential	Constant
1,3-dichloropropane	524.2		0.170	0.112	1.517	Exponential	Exponential
1,4-dichlorobenzene	502.2	ELCD	0.054	0.039	1.388	Exponential	Linear
1,4-dichlorobenzene	524.2		0.110	0.047	2.333	Exponential	Exponential
1-chlorobutane	524.2		0.200	0.058	3.451	Exponential	Linear
2,2-dichloropropane	524.2		0.700	0.117	5.985	Exponential	Hybrid
2-butanone	524.2		0.775	1.261	0.615	Exponential	Exponential
2-chlorotoluene	502.2	ELCD	0.184	0.104	1.776	Exponential	Exponential
2-chlorotoluene	502.2	PID	0.222	0.391	0.568	Exponential	Constant
2-chlorotoluene	524.2		0.121	0.036	3.343	Exponential	Exponential
2-hexanone	524.2		0.815	0.782	1.042	Exponential	Exponential
2-nitropropane	524.2		0.965	8.974	0.108	Exponential	Constant

Table 9. Comparison of 16-point and 5-point Single-laboratory IDEs (SL-IDEs) for the Episode 6000 Data Set							
Analyte	**Method**	**Procedure**	**SL-IDE (16)**	**SL-IDE (5)**	**SL-IDE(16)/ SL-IDE(5)**	**SL-IDE 16 Model**	**SL-IDE 5 Model**
4-chlorotoluene	502.2	ELCD	0.159	0.138	1.153	Exponential	Linear
4-chlorotoluene	524.2		0.102	0.039	2.648	Exponential	Exponential
4-isopropyltoluene	524.2		0.102	0.037	2.762	Exponential	Exponential
4-methyl-2-pentanone	524.2		1.060	0.987	1.074	Exponential	Exponential
Acetone	524.2		2.025	28.956	0.070	Exponential	Constant
Acrylonitrile	524.2		1.197	0.982	1.219	Exponential	Exponential
Allyl Chloride	524.2		0.203	0.070	2.915	Exponential	Hybrid
Aluminum	1620		198.565	70.438	2.819	Constant	Constant
Aluminum	200.8		12.004	21.862	0.549	Exponential	Constant
Ammonia as Nitrogen	350.3		0.013	0.038	0.336	Exponential	Constant
Antimony	1620		4.087	6.023	0.678	Constant	Linear
Antimony	200.8		0.018	0.293	0.062	Exponential	Constant
Arsenic	1620		1.463	2.175	0.672	Exponential	Constant
Arsenic	200.8		0.346	0.340	1.015	Exponential	Exponential
Barium	1620		1.762	1.558	1.131	Constant	Constant
Barium	200.8		0.079	0.071	1.120	Exponential	Constant
Benzene	502.2	PID	0.077	0.058	1.324	Exponential	Exponential
Benzene	524.2		0.115	0.030	3.907	Exponential	Exponential
Beryllium	1620		0.428	0.427	1.003	Exponential	Exponential
Beryllium	200.8		0.019	0.017	1.138	Exponential	Constant
Boron	1620		19.884	21.488	0.925	Exponential	Exponential
Bromobenzene	502.2	ELCD	0.729	0.343	2.122	Linear	Exponential
Bromobenzene	502.2	PID	0.048	0.025	1.947	Exponential	Exponential
Bromobenzene	524.2		0.175	0.156	1.125	Exponential	Exponential
Bromochloromethane	502.2	ELCD	0.462	0.029	15.797	Linear	Exponential
Bromochloromethane	524.2		0.309	0.396	0.780	Exponential	Exponential
Bromodichloromethane	502.2	ELCD	0.064	0.018	3.584	Exponential	Exponential
Bromodichloromethane	524.2		0.182	0.093	1.951	Exponential	Exponential
Bromoform	502.2	ELCD	1.450	0.023	62.020	Constant	Linear
Bromoform	524.2		0.350	0.247	1.417	Exponential	Exponential
Bromomethane	502.2	ELCD	6.993	0.731	9.569	Constant	Exponential
Bromomethane	524.2		0.238	0.148	1.610	Exponential	Linear
Cadmium	1620		0.184	0.200	0.922	Exponential	Exponential
Cadmium	200.8		0.011	0.015	0.735	Exponential	Constant
Calcium	1620		39.651	51.207	0.774	Linear	Constant

Table 9. Comparison of 16-point and 5-point Single-laboratory IDEs (SL-IDEs) for the Episode 6000 Data Set							
Analyte	**Method**	**Procedure**	**SL-IDE (16)**	**SL-IDE (5)**	**SL-IDE(16)/ SL-IDE(5)**	**SL-IDE 16 Model**	**SL-IDE 5 Model**
Carbon Disulfide	524.2		0.203	0.083	2.440	Exponential	Linear
Carbon Tetrachloride	524.2		0.258	0.166	1.549	Exponential	Linear
Carbontet+1,1-dcp	502.2	ELCD	0.062	0.049	1.274	Exponential	Exponential
Chloroacetonitrile	524.2		1.535	1.842	0.833	Exponential	Exponential
Chlorobenzene	502.2	ELCD	0.440	0.044	9.900	Linear	Exponential
Chlorobenzene	502.2	PID	0.062	0.058	1.083	Exponential	Exponential
Chlorobenzene	524.2		0.119	0.035	3.378	Exponential	Exponential
Chloroethane	502.2	ELCD	2.492	0.090	27.544	Constant	Linear
Chloroethane	524.2		0.336	0.239	1.403	Exponential	Exponential
Chloroform	502.2	ELCD	0.031	0.008	3.923	Exponential	Linear
Chloroform	524.2		0.203	0.111	1.829	Exponential	Exponential
Chloromethane	502.2	ELCD	0.204	0.499	0.409	Exponential	Constant
Chloromethane	524.2		0.215	0.148	1.456	Exponential	Exponential
Chromium	1620		0.478	0.728	0.657	Exponential	Constant
Chromium	200.8		0.393	0.473	0.830	Linear	Constant
Cis-1,2-dce+2,2-dcp	502.2	ELCD	0.043	0.027	1.575	Exponential	Exponential
Cis-1,2-dichloroethene	524.2		0.203	0.181	1.123	Exponential	Exponential
Cis-1,3-dichloropropene	502.2	ELCD	0.059	0.015	3.860	Exponential	Exponential
Cis-1,3-dichloropropene	502.2	PID	0.077	0.104	0.743	Exponential	Exponential
Cis-1,3-dichloropropene	524.2		0.158	0.103	1.536	Exponential	Exponential
Cobalt	1620		15.560	11.825	1.316	Exponential	Exponential
Cobalt	200.8		0.008	0.000	-133.113	Exponential	Exponential
Copper	1620		20.328	15.251	1.333	Constant	Constant
Copper	200.8		0.770	0.873	0.882	Constant	Constant
Dibromochloromethane	502.2	ELCD	0.418	0.380	1.098	Linear	Constant
Dibromochloromethane	524.2		0.253	0.192	1.315	Exponential	Exponential
Dibromomethane	502.2	ELCD	0.441	0.286	1.543	Linear	Constant
Dibromomethane	524.2		0.342	0.347	0.985	Exponential	Exponential
Dichlorodifluoromethane	502.2	ELCD	0.087	1.175	0.074	Exponential	Constant
Dichlorodifluoromethane	524.2		0.420	0.265	1.584	Exponential	Exponential
Diethyl Ether	524.2		0.340	0.314	1.082	Exponential	Exponential
Ethyl Methacrylate	524.2		0.244	0.243	1.003	Exponential	Exponential
Ethylbenzene	502.2	PID	0.075	0.048	1.571	Exponential	Exponential
Ethylbenzene	524.2		0.167	0.111	1.504	Exponential	Exponential
Hardness	130.2		2.152	4.687	0.459	Exponential	Constant

Table 9. Comparison of 16-point and 5-point Single-laboratory IDEs (SL-IDEs) for the Episode 6000 Data Set

Analyte	Method	Procedure	SL-IDE (16)	SL-IDE (5)	SL-IDE(16)/ SL-IDE(5)	SL-IDE 16 Model	SL-IDE 5 Model
Hexachlorobutadiene	502.2	ELCD	0.090	0.069	1.300	Exponential	Linear
Hexachlorobutadiene	524.2		0.263	0.208	1.265	Exponential	Exponential
Hexachloroethane	524.2		0.234	0.234	1.000	Exponential	Exponential
Hexchlobutadiene+naphthalene	502.2	PID	0.598	0.567	1.055	Exponential	Constant
Iron	1620		345.686	1021.716	0.338	Linear	Constant
Isopropylbenzene	502.2	PID	0.059	0.038	1.551	Exponential	Exponential
Isopropylbenzene	524.2		0.113	0.036	3.137	Exponential	Exponential
Lead	1620		2.317	2.831	0.819	Exponential	Constant
Lead	200.8		0.197	2.771	0.071	Exponential	Constant
M+p Xylene	502.2	PID	0.116	0.114	1.014	Exponential	Constant
M+p Xylene	524.2		0.127	0.033	3.846	Exponential	Exponential
Magnesium	1620		99.662	176.736	0.564	Exponential	Constant
Manganese	1620		6.531	4.363	1.497	Constant	Constant
Manganese	200.8		0.106	0.074	1.419	Constant	Constant
Mercury	200.8		0.062	0.014	4.550	Exponential	Hybrid
Methacrylonitrile	524.2		0.643	0.529	1.216	Exponential	Hybrid
Methyl Iodide	524.2		0.173	0.099	1.746	Exponential	Exponential
Methyl Tert-butyl Ether	524.2		0.195	0.154	1.266	Exponential	Exponential
Methylacrylate	524.2		0.549	0.551	0.995	Exponential	Exponential
Methylene Chloride	502.2	ELCD	2.727	-1.325	-2.057	Constant	Constant
Methylene Chloride	524.2		0.276	0.159	1.737	Exponential	Exponential
Methylmethacrylate	524.2		0.484	0.366	1.322	Exponential	Linear
Molybdenum	1620		2.917	5.783	0.504	Exponential	Constant
Molybdenum	200.8		0.262	0.005	47.826	Constant	Constant
N-butylbenzene	502.2	PID	0.139	0.049	2.819	Exponential	Linear
N-butylbenzene	524.2		0.136	0.052	2.605	Exponential	Exponential
N-propylbenzene	502.2	PID	0.089	0.100	0.889	Exponential	Constant
N-propylbenzene	524.2		0.231	0.050	4.596	Exponential	Hybrid
Naphthalene	524.2		0.175	0.180	0.968	Exponential	Exponential
Nickel	1620		23.784	40.205	0.592	Exponential	Constant
Nickel	200.8		0.076	0.068	1.124	Exponential	Constant
o-xylene	524.2		0.161	0.084	1.925	Exponential	Exponential
o-xylene+styrene	502.2	PID	0.111	0.145	0.769	Exponential	Constant
P-isoproptol+1,4-dcb	502.2	PID	0.153	0.143	1.068	Exponential	Constant
Pentachloroethane	524.2		0.337	0.419	0.805	Exponential	Linear

Table 9. Comparison of 16-point and 5-point Single-laboratory IDEs (SL-IDEs) for the Episode 6000 Data Set							
Analyte	**Method**	**Procedure**	**SL-IDE (16)**	**SL-IDE (5)**	**SL-IDE(16)/ SL-IDE(5)**	**SL-IDE 16 Model**	**SL-IDE 5 Model**
Sec-butylbenzene	502.2	PID	0.079	0.053	1.504	Exponential	Exponential
Sec-butylbenzene	524.2		0.132	0.038	3.422	Exponential	Exponential
Selenium	1620		1.915	1.757	1.090	Exponential	Exponential
Selenium	200.8		0.410	0.311	1.317	Exponential	Exponential
Silver	1620		10.219	11.118	0.919	Exponential	Constant
Silver	200.8		0.010	-0.030	-0.348	Exponential	Exponential
Sodium	1620		133.007	134.645	0.988	Exponential	Exponential
Styrene	524.2		0.119	0.045	2.676	Exponential	Exponential
Tert-butylbenzene	502.2	PID	0.073	0.049	1.498	Exponential	Exponential
Tert-butylbenzene	524.2		0.170	0.055	3.093	Exponential	Exponential
Tetrachloroethene	502.2	ELCD	0.051	0.045	1.119	Exponential	Exponential
Tetrachloroethene	502.2	PID	0.157	0.097	1.607	Exponential	Linear
Tetrachloroethene	524.2		0.379	0.526	0.721	Exponential	Linear
Thallium	1620		1.208	1.198	1.009	Exponential	Linear
Thallium	200.8		0.001	0.000	3.140	Exponential	Exponential
Thorium	200.8		0.003	0.000	7.428	Exponential	Constant
Tin	1620		1.200	4.383	0.274	Exponential	Exponential
Titanium	1620		5.238	19.982	0.262	Exponential	Constant
Toluene	502.2	PID	0.061	0.061	0.999	Exponential	Constant
Toluene	524.2		0.130	0.142	0.918	Exponential	Constant [1]
Total Phosphorus	365.2		0.013	0.011	1.219	Exponential	Exponential
Total Suspended Solids	160.2		2.877	2.131	1.350	Exponential	Exponential
Trans-1,2-dichloroethene	502.2	ELCD	0.065	0.061	1.069	Exponential	Linear
Trans-1,2-dichloroethene	524.2		0.255	0.072	3.531	Exponential	Hybrid
Trans-1,3-dichloropropene	502.2	ELCD	0.082	0.021	3.845	Exponential	Exponential
Trans-1,3-dichloropropene	502.2	PID	0.085	0.110	0.774	Exponential	Exponential
Trans-1,3-dichloropropene	524.2		0.204	0.127	1.613	Exponential	Exponential
Trans-1,4-dichloro-2-butene	524.2		1.182	1.205	0.981	Exponential	Exponential
Trichloroethene	502.2	ELCD	0.050	0.013	3.715	Exponential	Exponential
Trichloroethene	502.2	PID	0.096	0.080	1.189	Exponential	Exponential
Trichloroethene	524.2		0.288	0.329	0.875	Exponential	Linear
Trichlorofluoromethane	502.2	ELCD	1.997	0.660	3.025	Constant	Constant
Trichlorofluoromethane	524.2		0.307	0.290	1.059	Exponential	Exponential
Uranium	200.8		0.001	0.000	4.743	Exponential	Exponential
Vanadium	1620		10.063	8.643	1.164	Exponential	Exponential

Table 9. Comparison of 16-point and 5-point Single-laboratory IDEs (SL-IDEs) for the Episode 6000 Data Set							
Analyte	**Method**	**Procedure**	**SL-IDE (16)**	**SL-IDE (5)**	**SL-IDE(16)/ SL-IDE(5)**	**SL-IDE 16 Model**	**SL-IDE 5 Model**
Vanadium	200.8		0.845	0.987	0.856	Exponential	Linear
Vinyl Chloride	502.2	ELCD	3.521	0.369	9.543	Constant	Linear
Vinyl Chloride	524.2		0.295	0.180	1.641	Exponential	Linear
WAD Cyanide	1677		0.672	1.243	0.541	Linear	Constant
Xylene (Total)	524.2		0.111	0.030	3.735	Exponential	Exponential
Yttrium	1620		3.119	13.404	0.233	Exponential	Constant
Zinc	1620		4.415	6.661	0.663	Exponential	Constant
Zinc	200.8		1.497	5.061	0.296	Exponential	Constant

Note: ELCD or PID in the Procedure column indicates the photo-ionization detector (PID) or electrolytic conductivity detector (ELCD) in EPA Method 502.2

[1] Original model picked was Hybrid, but failed to converge

Summary Statistics for Table 9

	IDE(16)/IDE(5) (all analytes)	**IDE(16)/IDE(5) (same model used)**	**IDE(16)/IDE(5) (different models used)**
Number of Analytes	198	108	90
Minimum:	-133.113	-133.113	0.050
25th percentile:	0.876	1.072	0.564
Median:	1.270	1.419	0.919
75th percentile:	2.328	2.310	2.122
Maximum:	62.020	47.826	62.020

	Number of analytes	**Percent of analytes**	**p-value (for percent=50)**
SL-IDE (16) > SL-IDE (5) (all analytes)	133	67.17%	<0.0001
SL-IDE (16) > SL-IDE (5) (same model used)	91	84.26%	<00001
SL-IDE (16) > SL-IDE (5) (different models used)	43	48.31%	0.832